

SOLUBILIZATION AND SPORE RECOVERY FROM
SILICONE POLYMERS

A Thesis
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science

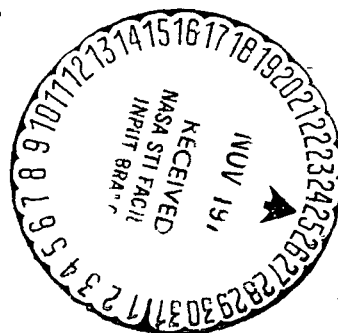
by

Yu-Chuan Hsiao

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

Department of Polymers and Coatings
College of Science and Mathematics

June, 1974
Fargo, North Dakota



APPROVAL OF THESIS

This thesis is approved by:

Loren W. Hill
Dr. Loren W. Hill, Advisor

June 25, 1974
(Date)

Zeno W. Wicks Jr.
Dr. Zeno W. Wicks Jr., Chairman
Department of Polymers and Coatings

June 25, 1974
(Date)

ABSTRACT

A non-sporicidal technique for solvent degradation of cured silicone polymers has been developed. This technique involves chemical degradation of cured silicone polymers by amine solvents at room temperature. Substantial improvements were obtained in the recovery of seeded spores from 'room temperature cured polymers' as compared to the NASA standard recovery procedures. This high recovery indicates that the curing process is not sufficiently exothermic to reduce spore viability.

The dissolution reaction of cured silicone polymers with amine solvents is proposed to occur by bimolecular nucleophilic displacement. That is, the amine acts as a nucleophilic reagent attacking preferentially at positive sites consisting of silicone atoms bonded to three oxygens, $\text{-O}-\overset{\text{O}}{\underset{\text{O}}{\text{Si}}}-\text{O}-$. Attack at silicon atoms bonded to two oxygens is proposed to be much slower. It is suggested that this selectivity explains why crosslinks are broken while straight chain segments are not depolymerized.

The dissolution of silicone polymers in amines suggested consideration of two applications, reclaiming used silicone polymers and applying silicone coatings to heat sensitive substrates which cannot be subjected to oven cure. Therefore, experiments were conducted to determine extent of recrosslinking on solvent evaporation, thermal stability and physical properties of reclaimed polymers, and film properties of room temperature cured coatings.

The chemical structure of silicone polymers was determined by spectroscopic methods. The phenyl to methyl ratio, R/Si ratio, molecular weight, and hydroxyl content of the silicone resins were determined.

DEDICATION

This thesis is dedicated to my wife and to my parents whose encouragement has made this thesis possible.

ACKNOWLEDGEMENT

The author wishes to express his deepest gratitude to Dr. Loren W. Hill for his advice and guidance given throughout the course of this work. Thanks are also due to Drs. B. P. Sleeper, S. P. Pappas and Z. W. Wicks for many valuable suggestions and helpful discussions in their respective fields.

The author also wishes to thank the National Aeronautics and Space Administration for funds made available and Dr. Lawrence Hall, NASA Planetary Quarantine Officer, for guidance and support.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	<u>1</u>
I. Detecting Buried Microorganisms within Solid Material	1
II. Definition of Silicone	5
III. Degradation of Silicone	6
STATEMENT OF THE PROBLEM	16
METHOD OF APPROACH	17
EXPERIMENTAL	20
I. Preparation of Starting Materials	20
A. Silicone Polymers	20
B. Solvents	20
C. Amines	22
D. Other Reagents	22
II. Structural Determination of Silicone Polymers	23
A. Determination of Hydroxyl Content	23
B. Infrared Spectroscopy Analysis	23
C. Nuclear Magnetic Resonance Analysis	23
D. Molecular Weight Determination	24
E. Determination of Phenyl to Methyl Ratio in Dow Corning Silicone Resins	26
(1) IR Method	26
(2) NMR Method	26
III. Preparation of the Cured Silicone Polymers	29
A. Silicone Resins	29
B. Silicone Rubbers	29
C. Determination of the Extent of Cure	29
IV. Physical Degradation of Cured Silicone Polymers	32
A. Solubility Parameter Determinations	32
B. Mechanical Degradation of Swollen Cured Polymer Samples	33
V. Chemical Degradation of Cured Silicone Polymers	33

VI.	Determination of Amine Toxicity	34
	A. Preparation of Broth Culture of <u>Bacillus subtilis</u>	34
	B. Determination of Viable Spore Population in Various Amines	34
VII.	Recovery Studies on the Silicone Potting Compounds	35
	A. Starting Materials	35
	B. Procedure	37
VIII.	The Solubilization of the Cured Silicone Polymers with Amine Solvents	40
	A. Determining the Degree of Degradation of Silicone Polymer in n-Butylamine by Viscosity Measurements	40
	B. Preparation of Silicone (DC 840) p-Nitrophenol Adduct	41
	C. Preparation of Silicone-Methanol Adduct	43
	D. Base-Catalyzed Siloxane Rearrangement Study at Room Temperature by Polymerizing Octamethyl-Cyclotetrasiloxane in Anhydrous Methanol	44
	E. The Effects of Solvent on the Solubilization of Cured DC 840 Silicone Resin by n-Butylamine	45
IX.	Physical Testing of Silicone Polymers	46
	A. Tensile Strength and Percent Elongation	46
	B. Degree of Crosslink	46
	C. Hardness Test	46
	D. Film Thickness Measurement	47
	E. Impact Resistance Test	47
	F. Chemical and Solvent Resistance Tests	47
	G. Thermodegradation Test	47
	H. Flexibility	48
	RESULTS AND DISCUSSION	49
I.	Structure of Silicone Polymers	49
II.	Physical Degradation of Cured Silicone Polymers	49
	A. Determination of Solubility Parameter for Cured Silicone Polymers	49
	B. Mechanical Degradation of Swollen Cured Polymer Samples	53

INTRODUCTION

1. Detecting Buried Microorganisms Within Solid Material

It is generally agreed that the search for extraterrestrial life is one of the most important objectives of the exploration of the planets (1, 2, 3, 4). Experimental analysis of possible extraterrestrial life forms could reveal basic differences in functions and chemical structure between these and terrestrial forms, thereby broadening our fundamental concepts of life. If we are to determine whether life does exist on other planets, we must not carry Earth life forms there during explorations. If life is found on another planet, we must be sure that it was present before we arrived, and not carried from Earth and placed there by our spacecraft. If a space probe contaminated with Earth organisms lands on another planet, that planet could become contaminated, and the opportunity to biologically assess it will be lost forever.

In order to prevent spreading organisms from our Earth environment, the National Aeronautics and Space Administration has placed contamination constraints on space probes. The Russian government is also concerned. An international planetary quarantine policy has been adopted. This policy requires sterility of planetary landers (5). This means that any spacecraft intended to land on another planet must apply the quarantine constraints to insure a low probability of

contamination during the period of exploration. In order to meet this requirement of providing a high degree of reliability of microbial decontamination, it is essential that methods for the detection of viable microorganisms be developed and that these be as sensitive and reliable as possible.

The detection of microorganisms which are trapped within solids constitutes a unique contamination control problem. Currently the method used to decontaminate spacecraft is a dry heat cycle. Bacterial spores encased in plaster of paris, various plastic potting materials, asbestos plastic cement, and solid rocket propellants are not exposed to high temperatures during the dry heat cycle for as long a period as those on surfaces (6). Due to this insulation from the effects of dry heat, it was deemed necessary to develop assay procedures which would allow the detection of very small populations of microorganisms within the solids. Some solids within the spacecraft may be subjected to temperatures in excess of sterilization requirements and thus constitute a minimum contamination control problem. There are, however, solid components which are adversely affected by such treatment. It is essential that the microbial population within these solid materials be accurately known in order to assess their contribution to the total contamination load of the entire spacecraft.

Methods which have been reported (7-13) for detecting buried microorganisms include: electron spin resonance, nonfluorescent staining, fluorescent staining, electrophoreses, autoradiography and culturing. It was found that with the exception of rather limited usefulness of fluorescent staining techniques, culturing represents the most useful, sensitive and easily applied method. Culturing depends on the ability of microorganisms to grow and reproduce when presented with proper nutrient environment. When microorganisms buried in solids are to be assayed by culturing, exposure from encasement is a key factor of the culturing method. Laboratory procedures which free organisms entrapped in solid materials fall into two major categories. One class of procedures requires that the material be broken into very small pieces (pulverized) so that microorganisms are exposed and colonies can grow and be counted. A second class of procedures requires that the material under investigation be dissolved in a suitable solvent which is non-toxic to the buried organisms.

The basic principle of the pulverization technique is to reduce the solid to particles of a size which would free all of the organisms present, but not damage the cells. The current pulverization of solid materials used in the fabrication of spacecraft is accomplished by the use of mortar and pestle, ball and vortex mills, high speed

blenders, drills, abrasive devices, saws and vacuum probes (8, 14-22). These methods each have their characteristic advantages and disadvantages. Control of the extent and uniformity of pulverization with these methods is difficult and in some cases not possible. The production of aerosols limits the usefulness of the high speed blenders and drilling techniques (23). With certain types of solids, explosions occur when the level of pulverization reaches a certain particle distribution range. The recovery of test organisms from pulverized solids using high speed blenders and drills was quite low (24). Petersen recently reported that use of the biodetection grinder resulted in 5.7% recovery from a seeded model system composed of laminated polystyrene; values of 0.1% recovery for seeded Eccobond had been reported previously (25). It is believed that the lack of adequate control of heat generated in these forms of pulverization as well as the physical rupture of the microorganisms may be responsible for such results.

Complete dissolution in a non-toxic solvent yields a higher recovery than grinding or pulverizing for material under investigation in general (26, 27). However very few types of materials can be dissolved without using combinations of heat, pressure and chemicals which may destroy the buried organisms. Rheineck and Heskin (28) studied a method for degrading amine cured epoxy resins which was

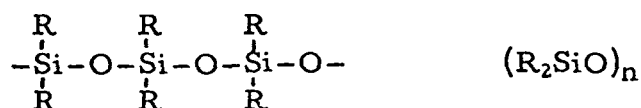
a composite of the mechanical pulverization by sawing and dissolution by solvent. This technique implemented the solubility parameter concept. They found that some solvents within a range of solubility parameters can dissolve cured epoxy resin without adding heat, pressure, or any chemicals. However this technique was not tested with actual culture methods. Mechanical pulverization by sawing prior to solvent dissolution may be harmful to viable microorganisms and reduce sensitivity of the detection technique.

This work was sponsored by NASA under the contract number NGR-35-001-012 and entitled "Quantitation of Buried Contamination by Use of Solvents". In a review of the "Non-metallic Materials Used on Spacecraft" published by NASA in 1968, various silicone resins and silicone rubbers are listed as the prevalent non-metallic material used (29), and a series of silicone resins and silicone potting compounds were chosen as the basis of this study.

II. Definition of "Silicone"

The term "silicone" is not used consistently in industry. It is sometimes employed generically to designate all monomeric and polymeric organosilicon compounds containing Si-C bonds. It can be used as a collective term for organosilicon polymers of all types. However, in this study, we restricted its usage to the organosilicon polymers containing Si-O-Si bonds. Accordingly, we define

"silicones" as organosilicon polymers in which the silicon atoms are bound to each other through oxygen atoms. If the silicon valences are not entirely taken up by oxygen, they are saturated by organic groups. The prototype for the simple linear polymers is thus built up according to the following scheme:

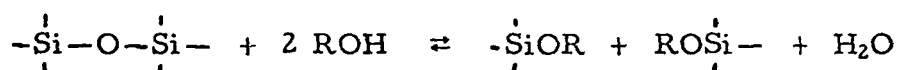


where R is an organic group.

III. Degradation of "Silicone"

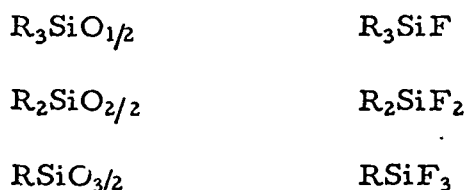
The degradation of "silicone" compounds has been investigated in several ways. Hyde, et al (30-32) found that high-molecular-weight siloxanes could be depolymerized at temperatures higher than 300°C and reduced pressures. Mixtures of cyclic polysiloxanes with $n = 3$ to 8 were obtained from polydimethylsiloxanes as products of thermal degradation at 350° to 400°C in vacuum. George and Zemaný (33) studied the thermal depolymerization of methylsilsesquioxane polymers $(\text{CH}_3\text{SiO}_{3/2})_n$ in the region of 250° to 600°C and at pressures above 100 mm Hg. They reported that considerable amounts of tetramethylsilane were obtained besides the hexamethyldisiloxane, hexamethylcyclotrisiloxane, methane, carbon monoxide, and carbon dioxide in the volatile degradation products.

The siloxane bond can be cleaved slowly by steam at high temperatures with the formation of siloxanol, according to Gebhardt, et al (34). They studied this type of degradation in a polydimethylsiloxane system by molecular weight determination. The initial molecular weight of 1,166,000 fell when the siloxane was heated in steam at 220°C as follows: after 2 hours, 155,000; after 3 hours, 133,000; after 4 hours, 87,000; and after 10.5 hours, 78,000. The variation of molecular weight with the temperature at a constant time of heating (4 hours) was as follows (initial molecular weight 1,050,000): 200°C, 338,000; 220°C, 70,300; 230°C, 33,000 and 240°C, 18,300. This reaction especially with the simultaneous use of alkaline catalysts is another route to the production of siloxanols, because of the good reproducibility of the molecular weights. Bailey (35) and Voronkov (36) studied a similar kind of degradation by heating and refluxing with high-boiling (120°-230°C) primary or secondary alcohols in the presence of an acidic (35) or alkaline (36) catalyst. They reported that siloxanes were converted into alkoxy siloxanes



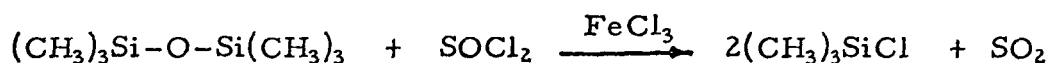
by continuous removal of the water evolved during the reaction. The degradation could be carried as far as the corresponding monomeric

alkoxysilanes. Humphrey, et al, (37, 38) found that high molecular weight polysiloxanes, such as silicone rubber polymers, could be degraded to low-molecular weight siloxanes by the action of hydrogen chloride. This degradation can be considered as an example of acid catalyzed depolymerization. Most acid catalyzed processes, however, lead to complete depolymerization with regeneration of the monomer. Booth and Freedman (39) found that the silicon-oxygen bond could be broken by stoichiometric amounts of anhydrous hydrogen fluoride in the presence of anhydrous copper sulfate as a catalyst. Addition of potassium or ammonium hydrogen fluoride to a sulfuric acid solution of the siloxanes cooled to 0°C (40), or heating with ammonium fluoride (41), produce the corresponding organofluorosilanes, from the reaction of the various siloxane units:



If a mixture or a copolymer of different siloxanes is used as the starting material, the organofluorosilanes corresponding to the silicone functionalities are obtained by this method. The products can easily be separated by distillation, and this offers a method of analysis of the polymer mixture (37). Lewis (42), in a patent, claimed that highly alkylated siloxanes, particularly hexamethyldisiloxane,

were also decomposed by thionylchloride in the presence of Friedel-Crafts catalysts and converted into the corresponding chlorosilanes in good yield. According to Lewis, when hexamethyldisiloxane is heated for 20 minutes in the presence of thionyl chloride in a molar ratio of 1:1.5 and 0.3% anhydrous iron III chloride, trimethylchlorosilane is formed in almost quantitative yield:



Patnode (43) and Sommer (44) in their studies found that the silicon oxygen bond in hexamethylsiloxane could be broken by stoichiometric quantities of sulfuric acid with the formation of trimethylsilyl sulfate,



and hexaethyldisiloxane could react similarly to form triethylsilyl-sulfate. Sauer (45) reported that trialkylsilyl phosphates were formed by the reaction of phosphorus pentoxide in equimolar ratio with hexamethyldisiloxane and hexaethyldisiloxane:

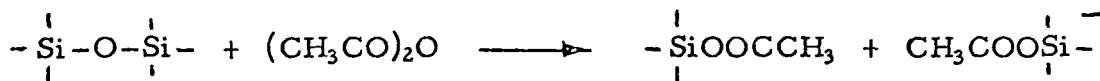


When an excess of phosphorus pentoxide is used, according to Feher (46), et al, solid trialkylsilyl polyphosphate is the main product:



Bailey, et al, (47) in their patent, claimed that in the presence of zinc chloride or sulfuric acid, siloxane can be decomposed to

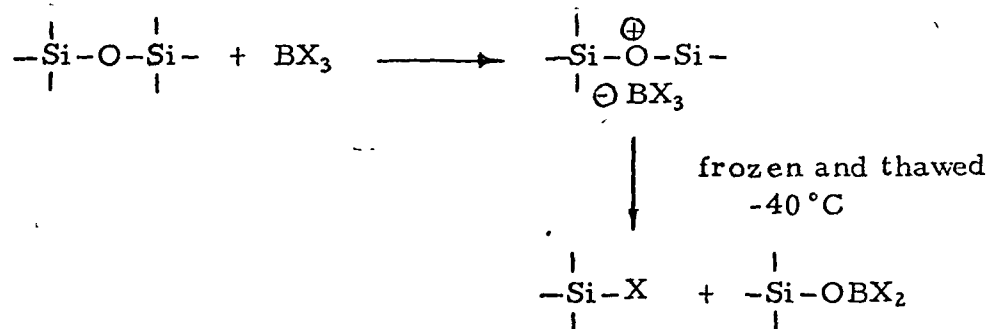
silicylacetate by acetic anhydride:



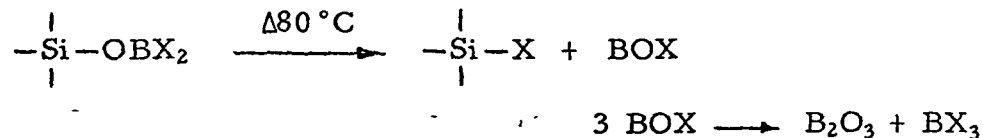
Hyde (48, 49) in a patented study reported that alkali metal hydroxides could catalyze depolymerization of polysiloxane at temperatures higher than 250°C. This degradation reaction is similar to purely thermal depolymerization. Even small amounts of NaOH, of the order of 0.1%, have a considerable effect. Polydiorganosiloxanes are degraded to the cyclic trimer $(\text{R}_2\text{SiO})_3$ and tetramers $(\text{R}_3\text{SiO})_4$. However, if the initial products contain triorganosiloxy groups, the hexaorganodisiloxanes are formed in the reaction products. Barry (50) in his patent, claimed that the alkali could depolymerize a cross-linked polymer containing $\text{RSiO}_{3/2}$ units and produce low molecular weight products. From these products low molecular-weight spherocyclic siloxanes $(\text{RSiO}_{3/2})_n$ could be isolated in low yield by distillation under reduced pressure. If stoichiometric ratios of alkali-metal hydroxides are used, alkali-metal silanates are formed from the reaction. The alkali-metal salts of tri-, di- or mono-organosilanols are formed, depending on the functionalities of the siloxane units present. Since these products have different solubilities, Hyde (51) reported that it is possible to use alkaline hydrolysis for the separation of polymers based on different siloxane units. The salts of monoorganosilanols are water soluble, while

the salts of di- and triorganosilanols hydrolyzed in water to give polysiloxanes soluble in organic solvents. The former can thus be extracted with water, and the latter can be taken up in organic solvents.

Lewis acids are also used in stoichiometric amounts for cleaving the siloxane bond. Organohalosilanes and heterosiloxanes are formed as a result of the decomposition. The cleavage of a siloxane bond by Lewis acids starts with the attachment of the acid to the siloxane oxygen which has two lone pairs of electrons which can act as an electron doner:

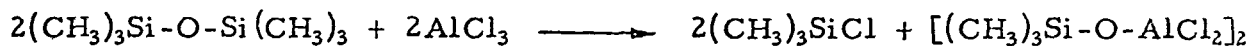


Examples of such scission of the siloxane bond that have been investigated by Emeleus (52) and McCusker (53) are the reactions with boron trifluoride and trichloride.

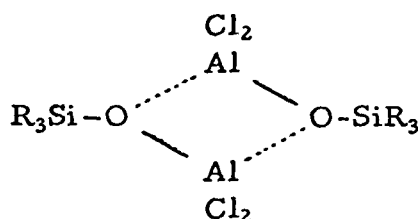


Hyde (54) used aluminum halides to cleave the siloxane bond and produced alkylsiloxyaluminum halides. Orlov (55) in his study shows

that hexamethyldisiloxane and aluminum chloride give trimethylsiloxyaluminum dichloride:



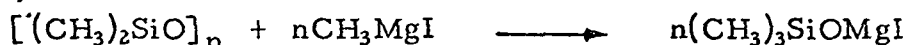
Schmidbaur (56) investigated the structure of the trimethylsiloxyaluminum dichloride. He reported that it is a dimer containing the almost planar skeleton as below:



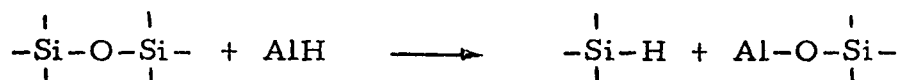
Andrianov (57), et al, found that the siloxane bond also can be ruptured by titanium tetrachloride at temperatures higher than 120°C. According to Andrianov, cleavage of hexaalkyldisiloxanes gives trialkylsiloxytitanium chlorides and small amounts of aluminum chloride have a catalytic effect (57):



Early in 1911, Kipping and Hackford (58) found that organo-metallic compounds could break the siloxane bond as demonstrated by the reaction of methylmagnesium iodide with polydimethylsiloxanes. Later, Sauer (59) found that a siloxanylmagnesium iodide was first formed and this could be converted into the silanol with water:



Analogously, Jenkner (60) found that polyorganosiloxanes could be decomposed by alkylaluminum compounds into lower molecular weight compounds that are more highly alkylated. Fritz(61) reported that a dropwise addition of linear polydimethylsiloxanes to a solution of lithium tetrahydroaluminate in ether and a gentle warming of the solution could initiate a reaction which could be detected by the evolution of gas. The gas was identified as $(CH_3)_2SiH_2$. He proposed that the reaction probably proceeded in such a way that the siloxane bond is converted into an alumosiloxane bond and silane was evolved:



All of the above degradations of silicone compounds involve at least one or more important factors making such degradations unfeasible for viable microorganism recovery. The first is a temperature factor. Hall and Swenson (62) reported the length of time required to sterilize a body at given temperature is a function of the temperature experienced. At a temperature of $105^\circ C$ microorganism death occurs very slowly. At $125^\circ C$, about 24 hours are required to kill eight decades of spores and as the temperature reaches about $204^\circ C$, sterilization occurs in seconds or less.

Thermal depolymerization or degradation by steam and alcohols required temperatures as high as 200°C to 600°C. Such degradations can sterilize the polymer within seconds and none of the microorganisms can survive in the degradation process.

The second factor is that many of the chemicals involved in degradation reactions are likely to be toxic. Reagents such as hydrogen fluoride, thionyl chloride, boron tribromide, methyl magnesium iodide, etc., are halogen compounds; these are generally oxidizing agents and are very toxic to microorganisms. The reason for this is that all forms of microorganisms depend on protein, both enzymatic and structural, for continued life and that the halogen compounds will oxidize and react readily, rapidly and destructively with proteins. The nucleic acids are also potential targets for halogen compounds. In general vegetative cells are killed rapidly. Knox, et al (63) has produced evidence to suggest that enzymes containing SH groups are especially sensitive targets for chlorine in the bacterial cell. Strong acids or bases such as hydrogen chloride, sulfuric acid, sodium hydroxide, potassium hydroxide, etc. (64), are also harmful to microorganisms. To maintain enzymatic activity, spore survival is restricted to a relatively narrow pH range, usually around 7. Thus, excess acid or base inside a cell will prove harmful to the enzymic reactions preventing growth or seriously damaging

the cell.

Other extremely reactive chemicals such as phosphorus pent-oxide, lithium and aluminum compounds are also toxic to micro-organisms.

Combinations of heat, pressure and toxic chemicals eliminate the use of all degradation techniques available in the literature. Acid or base catalyzed degradations, cleavage with organometallic compounds, lithium tetrahydroaluminate and Lewis acids, for reasons mentioned above, could not be used.

STATEMENT OF THE PROBLEM

This work was sponsored by NASA under the contract number NGR-35-001-012. The project was entitled "Quantitation of Buried Contamination by Use of Solvents". The objectives described in this thesis were to attempt to answer the problems posed by this grant:

- 1) development of a non-sporicidal technique for solvent degradation of cured polymeric resins, especially silicone rubbers and silicone resins that are used in spacecraft; and
- 2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated.

As the project developed, it became clear that solubilization would be possible and as a result another objective was adopted; that is to determine how effectively a silicone polymer could be recrosslinked after solubilization of the original cured polymer. This objective is related to the possibility of recovery and recycling of silicone polymers.

METHOD OF APPROACH

The choice of method used to degrade the polymer and release the encased microorganisms was severely restricted by the requirement for a non-destructive effect on the encased microorganisms. Possible methods included either a combination of solvent swelling and mechanical force or degradation of the cured polymer by a non-toxic chemical. A crosslinked polymer is not normally soluble in any solvent unless the solvent reacts with the polymer to break the chemical bonds responsible for crosslinking. However, crosslinked polymers may swell to many times their original volume by absorbing certain solvents; this swelling reduces the mechanical strength. Therefore, it appears very likely that mechanical degradation of the swollen silicone polymers could be achieved with less severe grinding than is required for the dry polymers. Hopefully such grinding will minimize the damage to the spores during the degradation process.

The problem of selecting a certain solvent to swell a given polymer can be greatly facilitated by using the solubility parameter approach (65, 66). The solubility parameter concept is based on thermodynamics of regular solutions. Application of this concept permits prediction of solvents which will be best for dissolving or swelling the polymeric solid. For crosslinked polymers, a solvent having a solubility parameter close to that of the polymer will cause swelling rather than complete solubilization (66). The solubility parameter range of

silicone polymers can be obtained from the manufacturer or by experimental determination. A solvent having a solubility parameter within the solubility parameter range of the polymer can be predicted to cause swelling. Among the many solvents having the required solubility parameter, those that are reported to be non-toxic or less toxic can be used to develop a method for recovery of spores from inoculated silicone polymers.

According to Pauling, silicon has an electronegativity of 1.8, carbon 2.5, nitrogen 3.0, oxygen 3.5, and hydrogen 2.1. Thus silicon is the most electropositive of the above elements, and therefore, many silicon linkages have rather pronounced ionic characters and greater bond polarizability than is true for analogous bonds involving carbon. An attacking reagent can thus induce a charge separation in a silicon-oxygen bond more easily than in a carbon-oxygen bond. Because of these factors, silicon-oxygen bonds are apt to undergo heterolytic rather than homolytic fission. As mentioned in the literature, cleavage of silicon-oxygen bonds in a condensed liquid phase always proceeds either by nucleophilic attack on silicon or electrophilic attack on oxygen. Existing methods for degradation of the cured silicone systems of concern in this study are discussed above. The use of these methods is precluded due to the effect of experimental conditions and reagent toxicity on the microorganisms. However,

there is a possibility of finding a non-toxic or less toxic nucleophilic reagent capable of degrading the cured silicone polymers under the temperatures and pressure limitations imposed. The experimental approach utilized in this study was determined by the factors discussed above.

EXPERIMENTAL

I. Preparation of Starting Materials

A. Silicone polymers

Three types of silicone polymers were used:

- 1) silicone oils
- 2) silicone rubbers
- 3) silicone resins

The silicone polymers were obtained from the Resins and Chemical Division of Dow Corning Corporation (DC-200, 801, 802, 803, 804, 806A, 808, 840, Silastic J) and General Electric Company (SR-112, RTV-41, 60). To maintain the original conditions, the prepolymers used as starting materials were not purified or modified in anyway. Typical properties of the silicone resins and silicone rubbers are listed in Table I.

B. Solvents

A series of solvents of increasing solubility parameter was obtained for each class of hydrogen bonding (66). In order to avoid the effect of water and other impurities in the solvents, all the solvents were dried over anhydrous sodium sulfate and purified by distillation.

Table 1. Properties of Silicone Polymers (67, 68)

	ASTMD 115-55 Solid content, %	Solvent	Specific gravity (25°C) average	Suggested Curing Time 1 hour	Viscosity at 25°C centipoises	Color Gardner
Dow Corning						
801 resin	60	Xylene	1.05	480°F	100 to 300	2
802 resin	50	Xylene	1.01	480°F	100 to 200	2
803 resin	50	Xylene	1.03	480°F	100 to 200	2
804 resin	60	Toluene	1.06	450°F	20~40	1
806A resin	50	Xylene Toluene	1.03	480°F	100~200	1
808 resin	50	Xylene	1.01	480°F	100~200	2
840 resin	60	Toluene	1.06	450°F	15~20	1
General Electric SR-112	50 ± 1	Xylene	1.01	480°~500°F	75~150	0-3
General Electric Rubber RTV-41	100%	none		room temp	400 pourable	white
RTV-60	100%	none		room temp	500 pourable	red
Dow Corning Rubber Silastic "J"	100%	none		room temp		green
Dow Corning 200 Fluid	100%	none			2.0 and 100	1

C. Amines

Amine solvents were dried and purified by refluxing 500 gms of the reagent grade amine over 20 gms of phosphorus pentoxide under a nitrogen atmosphere and then distilling twice. The fraction obtained within $\pm 1^\circ\text{C}$ of the boiling point was collected directly in a dried automatic dispensing container which contained 30 gms of dry Linde molecular sieves.

D. Other Reagents:

1. p-Nitrophenol (Eastman Organic Chemical) was purified by sublimation at 100°C , 0.2 mm Hg.
2. Diethylether anhydrous (Fisher Scientific-analytical grade).
3. Octamethylcyclotetrasiloxane (D_4) was obtained from Alfa Inorganic, Beverly, Massachusetts. The D_4 was dried over calcium hydride and redistilled, b.p. 175°C at 760 mm ($n_{\text{D}}^{20} = 1.3968$ (69, 70)).

II. Structural Determination of Silicone Polymers

A. Determination of Hydroxyl Content (71)

The hydroxyl content of silicone prepolymers was determined by weighing from 1 to 2 grams of the sample in a 125 ml glass stoppered flask; 5 ml of 2M acetic anhydride in pyridine was added with good stirring. The reaction was allowed to proceed at least 5 minutes at room temperature; then 2 ml of water was added followed by 10 ml of a 3 to 1 pyridine-water solution. The flask was allowed to stand for 5 minutes; then the solution was titrated with 0.5 N NaOH in methanol to an apparent pH of 9.8 using glass-calomel electrodes and a pH meter. A blank determination was also run. The difference between the blank volume and the sample titration volume was used to calculate the percentage of hydroxyl groups in the sample.

$$\% \text{ Hydroxyl} = \frac{(\text{Blank-sample titer in ml})(N \text{ of NaOH})(m. w. \text{ of OH})}{\text{wt. of sample in milligrams}}$$

B. Infrared Spectroscopy Analysis

The infrared (IR) spectra were taken on Perkin Elmer 137 and 441 spectrophotometers using sodium chloride plates. Samples were run as dry films.

C. Nuclear Magnetic Resonance Analysis

Nuclear magnetic resonance (NMR) spectra were determined with a Varian model A-60A, 60-megacycle analytical NMR spectrophotometer.

The samples were prepared from 30 to 50 weight percent in CDCl_3 unless otherwise specified. Tetramethyl silane (TMS) or benzene, with a peak position of δ 7.37, was used as an internal reference.

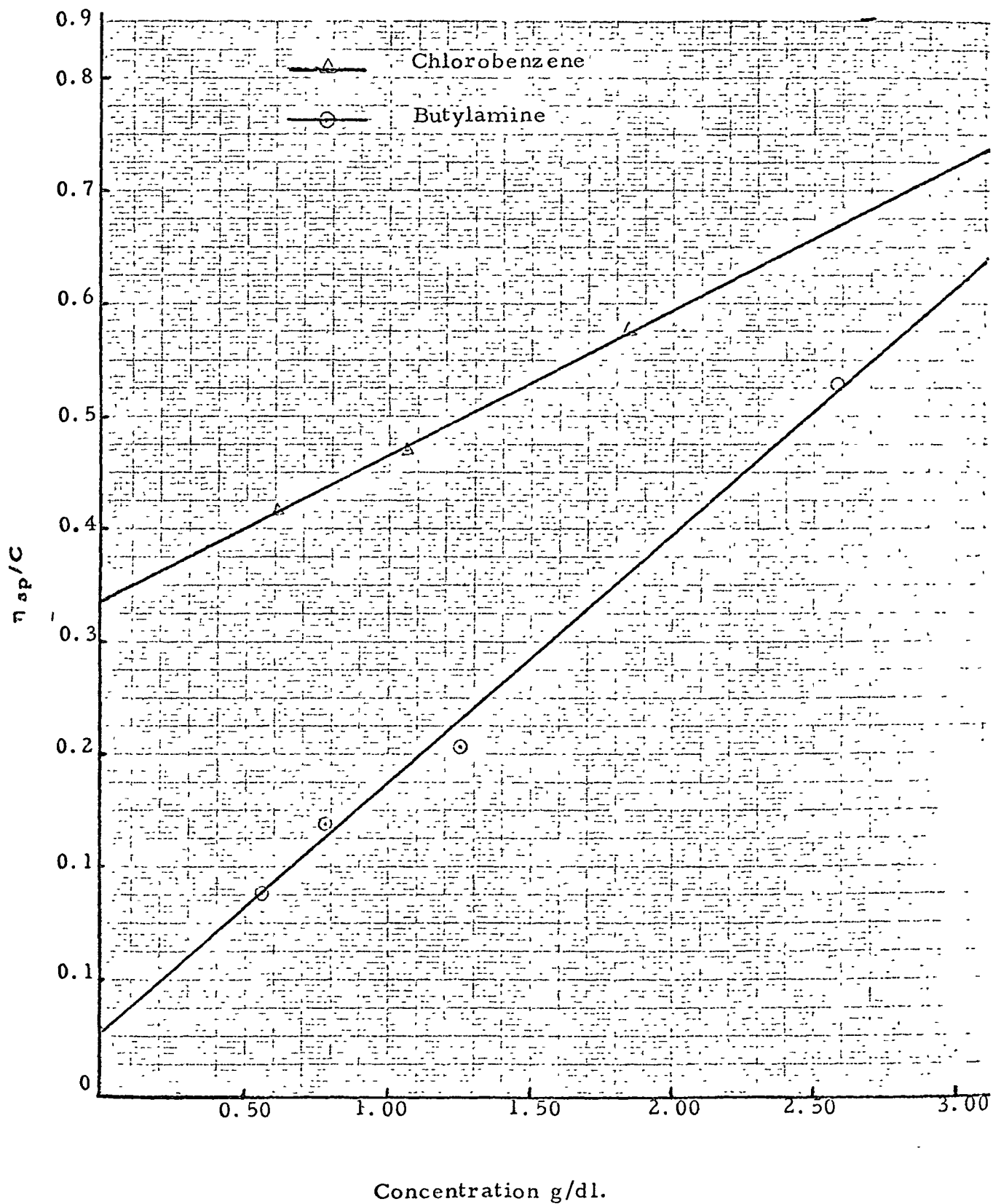
D. Molecular Weight Determination

The number average molecular weights (\overline{M}_n) (72) were determined with the Mechrolab Vapor Pressure Osmometer, Model 301A. Analytical grade methylethyl ketone was used as solvent. Benzil was used to determine the standard calibration curve for the instrument. An equilibration time of two minutes was used. The molecular weight was extrapolated to zero concentration by plotting the molecular weights vs. a series of concentrations ranging from 1.5×10^{-3} to 12.5×10^{-3} molality.

A molecular weight determination was also carried out by a polymer solution viscosity method using the Cannon-Fenske viscometer, size 50, in a constant temperature bath (45°C). The intrinsic viscosity of the DC 840 prepolymer sample was determined by making four measurements of the specific viscosity of the polymer at 3 concentrations. The values obtained were plotted as (specific viscosity/concentration) vs. concentration as shown in Figure I. The intrinsic viscosity was obtained by extrapolation. The Mark-Houwink equation was used to calculate the molecular weight (\overline{M}_v). This equation defines the relationship between intrinsic viscosity and molecular weight

$$[\eta] = K \overline{M}_v^a$$

Figure I. Reduced Viscosity vs. Concentration Curves for
DC840 Prepolymer in Chlorobenzene and
Butylamine



E. Determination of Phenyl to Methyl Ratio in Dow Corning Silicone Resins

(1) Infrared Method

Determination of the phenyl to methyl ratio in siloxane polymers was accomplished with the infrared spectroscopy method of Grant and Smith (73). According to this method, the phenyl/methyl ratio may be measured by determining the ratio of peak areas for the key absorption bands at 3.2 and 3.4 μ , respectively. A calibration curve taken from Grant and Smith was used. The calibration consisted of a plot of $\log (A_{3.2}/A_{3.4})$ versus $\log \phi/\text{CH}_3$ as shown in Figure II. Measurements were made with a Perkin-Elmer, Model 421 infrared spectrometer using thin films on NaCl discs. A planimeter (K and E 4236) was used to measure the peak areas.

(2) NMR Method

The direct proportionality of peak areas to the number of the hydrogen atoms was used to determine the phenyl/methyl ratios in the siloxane polymers (74, 75). NMR spectra were determined with a Varian Model A-60A, 60 megacycle analytical spectrophotometer. Dioxane with a single peak at δ 3.70 was chosen as an internal reference. Three well separated peaks appeared as shown in Figure III. In addition to the NMR electronic integrator, a planimeter (K and E 4236) was used to measure the peak areas.

FIGURE II

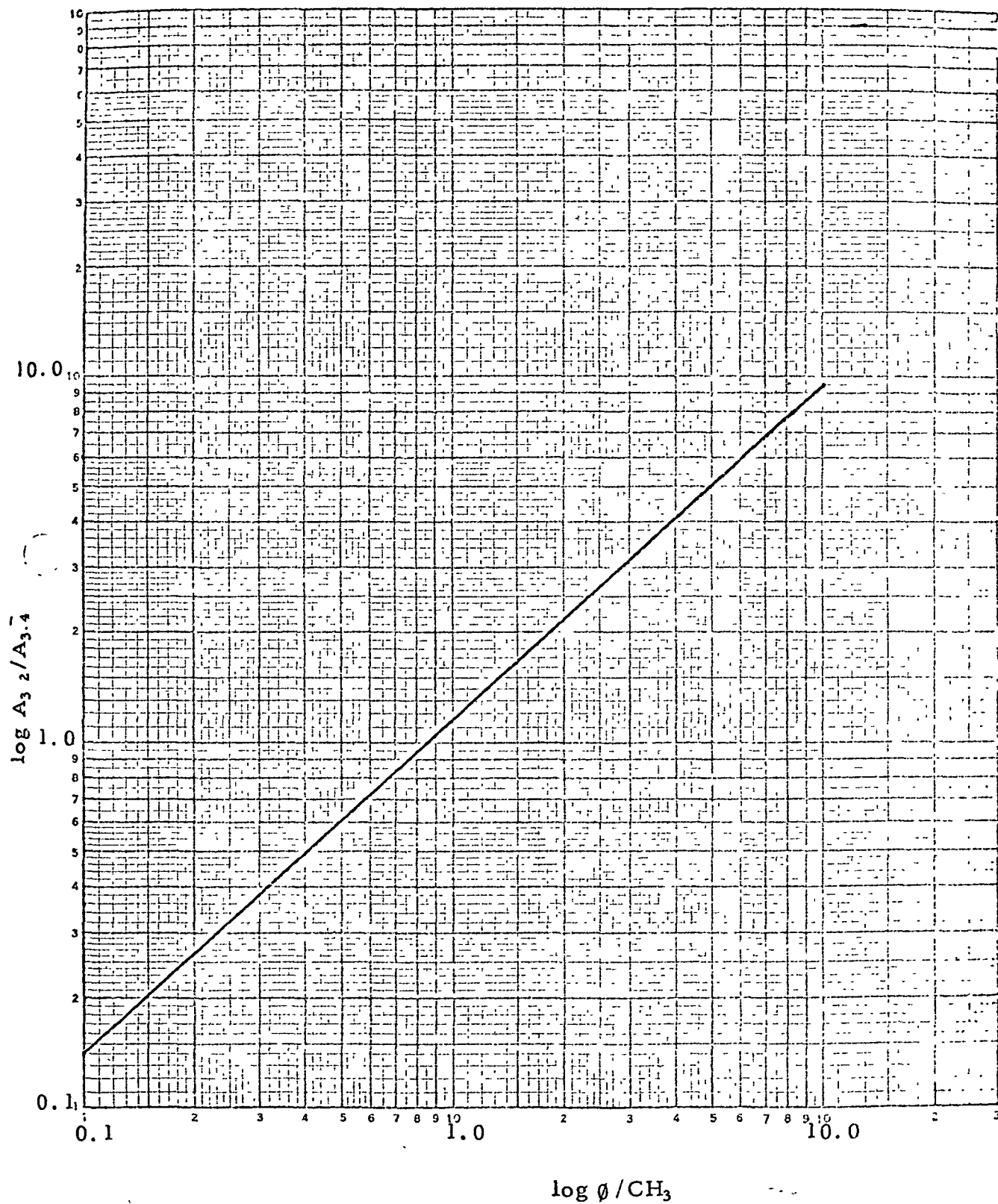
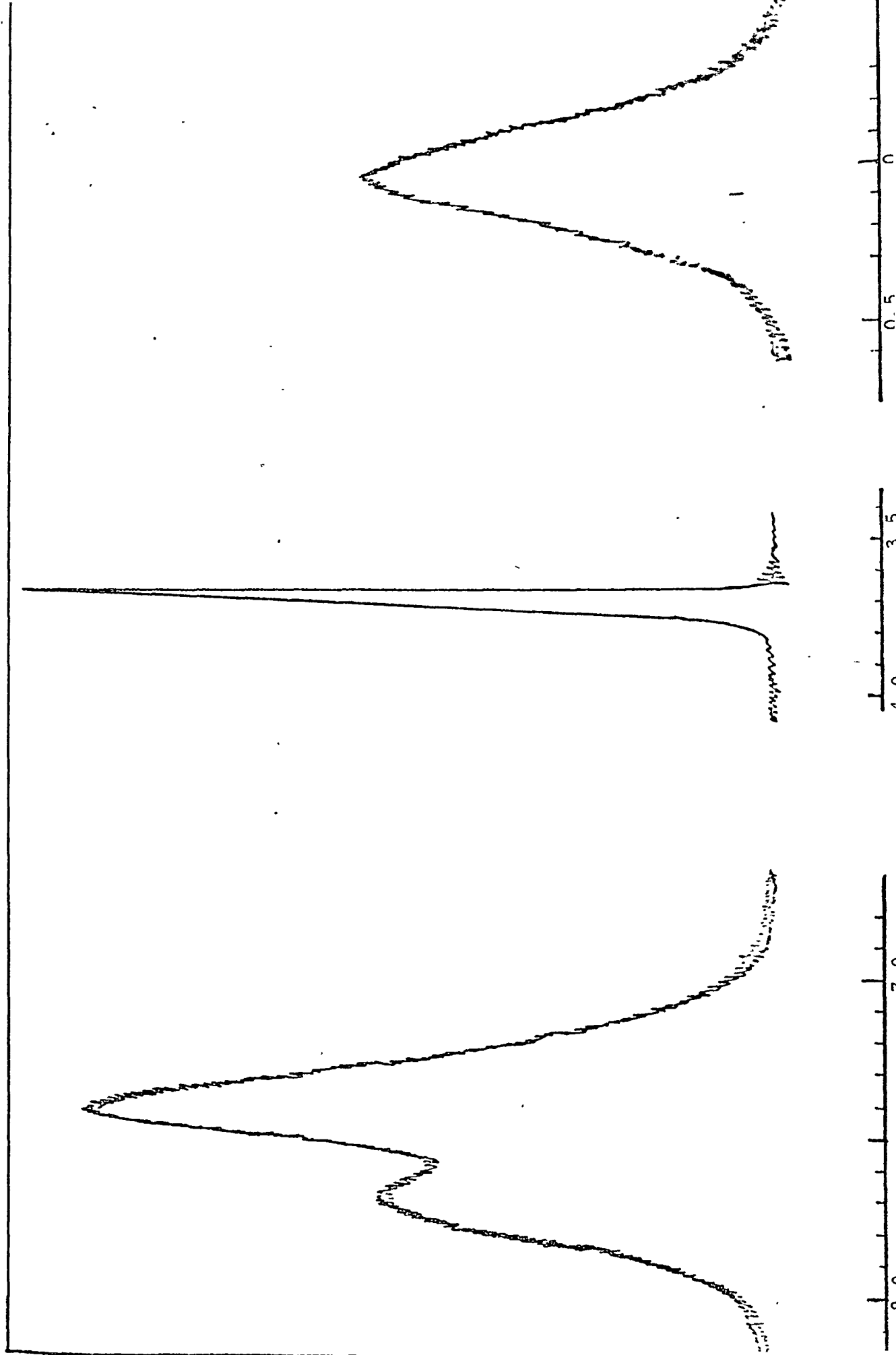
Standard Curve for Determining the ϕ/CH_3 Ratio (73)

Figure III. Nuclear Magnetic Resonance Spectrum of Binary Mixtures
Containing Organosiloxanes Recorded at 60 Mc and 36°C



III. Preparation of the Cured Silicone Polymers

A. Silicone Resins:

All of the cured silicone resin samples were prepared using the following procedure. The silicone resin prepolymer was placed in an aluminum dish and kept at room temperature for 24 hours to evaporate the solvent. Samples were then cured at high temperature. The recommended curing time for silicone resins is one hour at 450-480 °F (232-249 °C). In order to obtain better cure, the resins were baked at 480 °F (249 °C) for two hours. The samples were ground to a particle size of less than 0.1 cm in diameter by means of mortar and pestle.

B. Silicone Rubbers

The cured silicone rubber samples were prepared by charging silicone prepolymer, 5.0 grams, to a 50 ml beaker and immediately adding 5 drops of the curing agent (dibutyl tin dilaurate). This ratio of prepolymer and curing agent corresponds to the supplier's recommendations. After 24 hours curing time, the samples were cut to 0.3 cm cubes using a razor blade.

C. Determination of the Extent of Cure

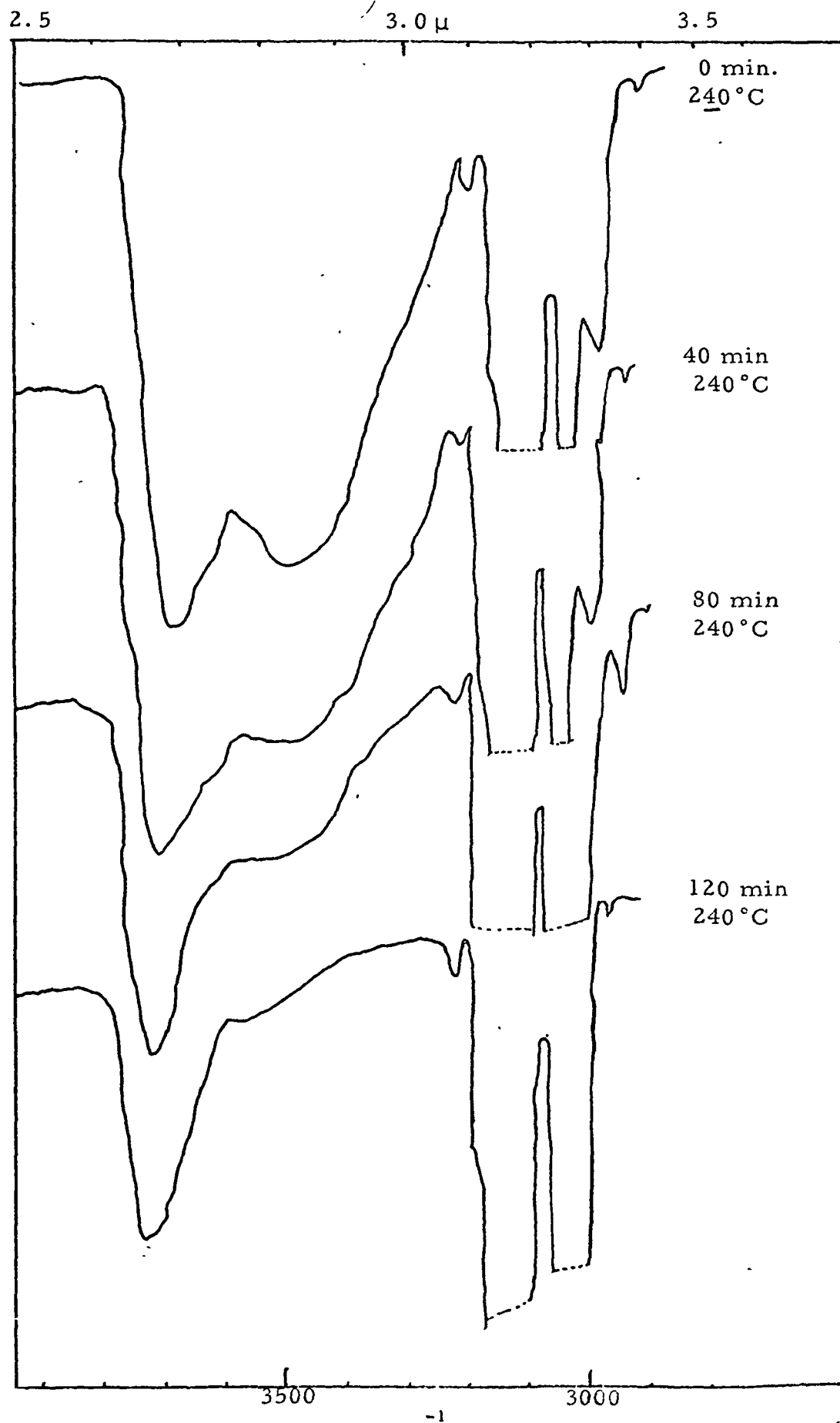
The extent of cure was obtained by analyzing for hydroxyl content with a Perkin-Elmer model 421 spectrophotometer. The prepolymer samples were examined as a pressed disc and as a deposited glassy film.

Thin films of each silicone resin prepolymer were deposited on six sodium chloride plates. The films were air dried for 10 hours, and then dried at 0.5 mm Hg vacuum (room temperature) for 3 hours. The first IR spectrum was taken immediately after the drying by vacuum. The sample plates were baked at 242°C (480°F). The first sample plate was withdrawn after 20 minutes, and subsequent samples were removed at 20 minute intervals. Each sample plate was then placed in the desiccator while cooling to room temperature.

The second method of preparing the samples for this analysis involved taking samples of silicone resins cured for different times and pulverizing them with a mortar and pestle. The pulverized samples were ground with potassium bromide and pressed to form a pellet for analysis.

The important areas in the spectra are shown in Figure IV. The decrease in the hydroxy absorbance is directly related to the extent of cure. The curing process involves reaction of two hydroxy groups to form one Si-O-Si bond. Thus the absorption corresponding to the OH stretching at $2.7\ \mu$ and the deformation vibration at $11\ \mu$ (76) decreases. Study of the stretching vibration has been used in the infrared spectroscopic study of the condensation of silicone resins containing OH groups by Damm and Noll (77) with good results.

Figure IV. Decrease in the OH Content During the Thermal Condensation of a Silicone Resin Shown in the IR Spectrum by the Behavior of the 3 and 2.7 μ absorptions.



IV. Physical Degradation of Cured Silicone Polymers

A. Solubility Parameter Determinations

The solubility parameter ranges of the cured silicone polymer samples were determined by Burrell's solvent spectrum method (66) as well as Rheineck and Heskin's approach (28). A series of purified solvents of increasing solubility parameters was obtained for each class of hydrogen bonding. The solvents for the spectra have been selected so that their δ values increase more or less uniformly from minimum to maximum values in any one of the three hydrogen-bond groups.

The cured silicone samples were weighed into a 10 mm by 75 mm pyrex test tube. The solvent was added by means of a pipet to make a 2% solution by weight. The solvent in the test tubes was frozen with dry ice, and then the tubes were sealed with a gas-oxygen torch.

The test tubes, each containing a sample, were placed in a 60°C constant temperature bath. The 60°C temperature is non-destructive to microorganisms (62). The samples were agitated for 48 hours and then inspected visually for swelling or dissolution.

The solubility parameter ranges of the silicone resin DC 840 prepolymer were determined by the same technique. The silicone resin prepolymer was heated to drive off the solvent, and the solubility parameter ranges were determined. The prepolymer DC 840 samples can be dissolved in the following solvents:

class I (poorly H-bonded)	8.0 - 10.5
class II (moderately H-bonded)	8.0 - 10.5
class III (strongly H-bonded)	9.5 - 12.5

The degree of swelling of cured silicone resin can also be determined by a similar technique. Samples of films were weighed (0.2 grams) and then allowed to swell in each solvent at room temperature for one week. Samples were checked periodically to determine when the samples reached swelling equilibrium. After this period, the sample films were removed from the solvent and weighed after air drying for two minutes. The percent swelling was calculated as follows:

$$\% \text{ swelling} = \frac{\text{Weight of solvent in sample polymer (grams)}}{\text{Weight of sample polymer (grams)}} \times 100$$

B. Mechanical Degradation of Swollen Cured Polymer Samples

After cured polymer samples had been swollen in a suitable solvent for 48 hours at 45°C, mechanical forces were applied to disperse the sample. This was accomplished through the use of high speed blenders as well as mortar and pestle.

V. Chemical Degradation of Cured Silicone Polymers

Due to the requirement of non-sporicidal degradation, all of the chemical degradation experiments were carried out at room temperature and atmosphere pressure. Nucleophilic reagents were used as solvents. The size of cured silicone polymer samples was reduced to less than 3 mm cubes, by means of mortar and pestle or razor blade. The silicone polymer samples were weighed (0.05 grams) into

a 5 ml screw capped clear glass vial, and 2 ml of nucleophilic reagent was then added. The solubilization was assisted by placing the sample on an automatic shaker for 48 hours at room temperature. The sample was then inspected visually for swelling or dissolution.

Strong bases such as potassium hydroxide, cesium hydroxide, rubidium hydroxide, sodium hydroxide, lithium hydroxide, as well as amines were used as the nucleophilic reagents. The hydroxides were dissolved in anhydrous methanol (2% by weight PH - 13). The amines were purified as described above.

VI. Determination of Amine Toxicity

A. Preparation of Broth Culture of Bacillus Subtilis

A nutrient agar slant culture of Bacillus subtilis was obtained from Dr. B. P. Sleeper in order to determine whether amine solvents were toxic to bacterial spores. The culture was transferred to a fresh nutrient agar slant and incubated at room temperature for three days. From the three-day slant 25 ml of nutrient broth (Difco) in a 250 ml flask was inoculated and incubated on a shaker at 30°C for 48 hours. Spore formation was detected microscopically. Spore aggregates were dispersed in a Sorvall Omni Mixer (Ivan Sorvall Inc., Norwalk, Conn), spread setting 5, for one minute.

B. Determination of Viable Spore Population in Various Amines

The broth suspension of *B. subtilis* spores was heat treated at 55°C for 15 minutes. Then one ml of heat treated suspension was transferred

to each of 5 test tubes containing 9 ml of diluent. The control diluent was sterile distilled water; the other tubes contained 9 ml of various amines in sterilized test tubes. The diluted sample (1:10) was shaken well and time zero was recorded. Serial dilutions were prepared in sterilized distilled water and appropriate dilutions were plated on five replicate nutrient agar plates in two different ways: 1) by mixing one ml with tempered nutrient agar (45°C) with gentle swirling before solidification and 2) by spreading one ml over the surface of each plate after agar solidification. The plates were inverted and incubated for 4-5 days at 30°C. Plates which had between 30 and 300 colonies were selected for carrying out colony counts. Counting was done by inverting the plate on a colony counter and marking with a wax crayon as each colony was counted. Recorded counts are the average of the 5 replicate plates. The protocol of the above procedure is illustrated in Figure V.

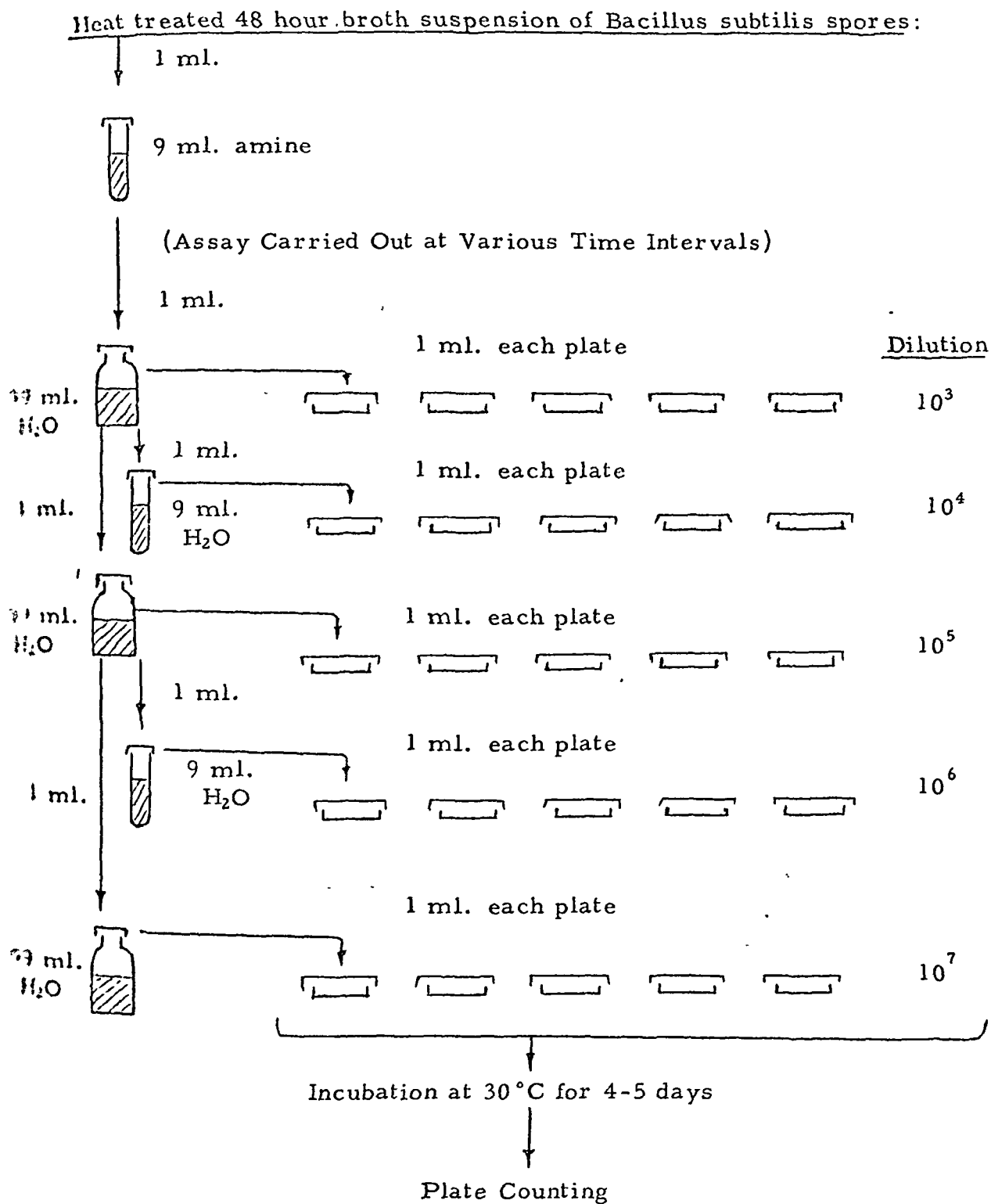
VII. Recovery Studies on the Silicone Potting Compounds (RTV 41, RTV 60)

A. Starting Materials

n-Butylamine - Eastman Organic Chemicals reagent grade distilled.

Spore Suspension - Bacillus subtilis var. niger
ca. 10^8 /ml in 95% ethanol-produced in
SSM-10 liquid sporulation medium.
Designation "BGSSM-10". Obtained
from Dr. Walter W. Bond, Experimental
Microbiology Unit, Environmental
Microbiology Section, US DPHA, DHEW,
Phoenix, Arizona.

Figure V. Protocol for Determination of Spore Viability after Treatment with Amines.



Liquid Silicone Rubber, RTV-41 (Lot No. BE 180), RTV-60 (Lot No. BC 624) - General Electric, Silicon Products Department, Waterford, New York.

RTV Silicone Rubber Curing Catalyst - Dibutyl Tin Dilaurate - General Electric.

Benzene - Baker Chem. Co., reagent grade, Lot no. 9154.

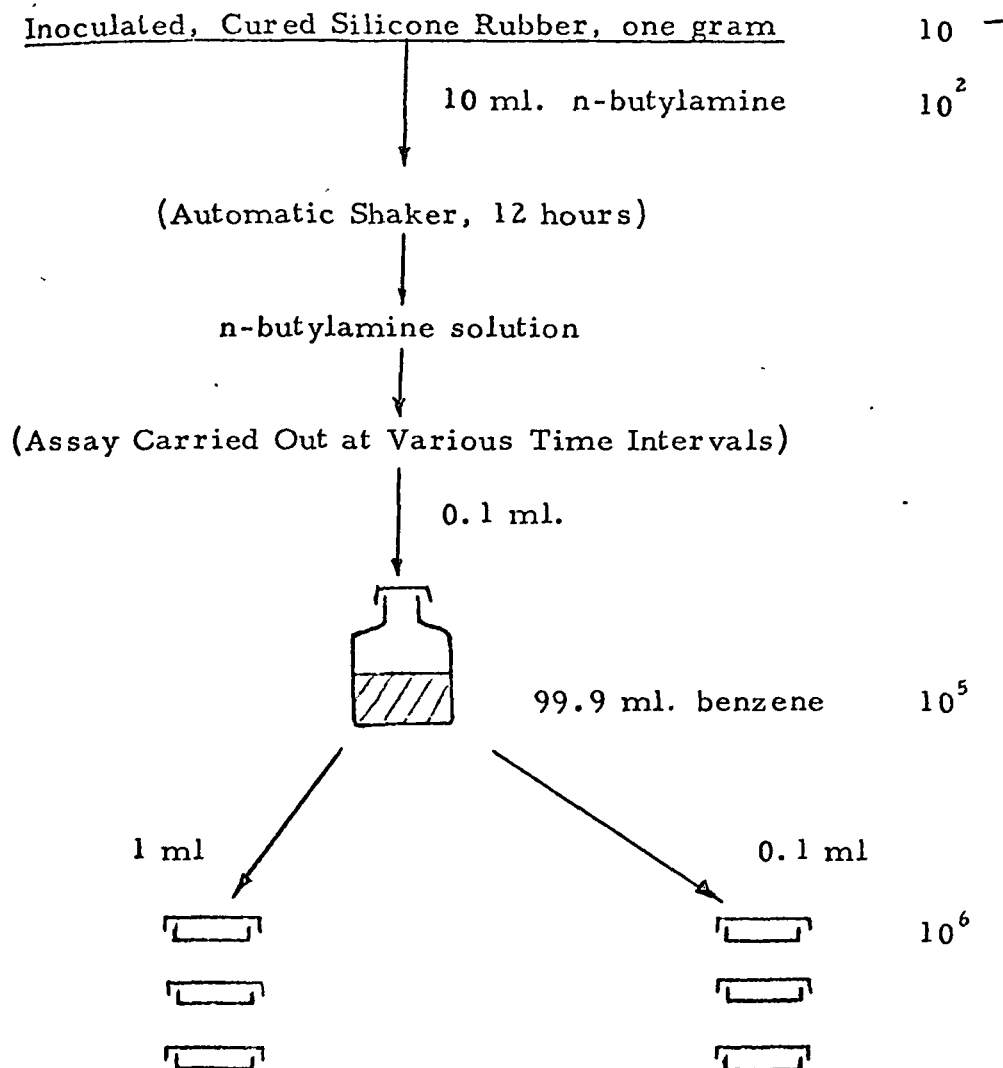
Tryptic Soy Agar (dehydrated) Control 577932 - Difco Laboratories, Detroit, Michigan.

B. Procedure

An inoculated silicone rubber potting compound was prepared from the following:

- | | |
|--|----------|
| (a) Silicone prepolymer, (RTV 41, RTV 60) | 1.0 gram |
| (b) Curing agent (dibutyl tin dilaurate) | 1 drop |
| (c) Spore suspension (10^8 /ml. in 95% ethanol) | 0.10 ml |

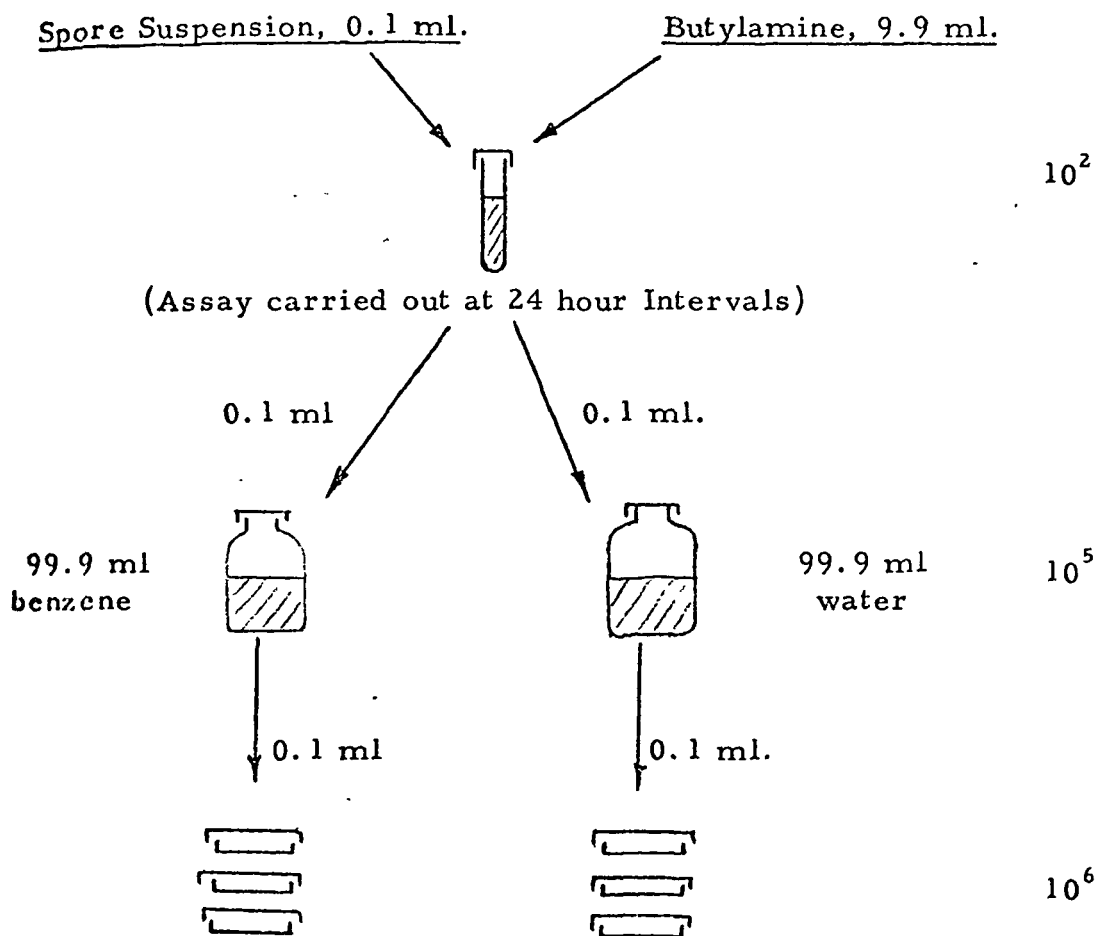
The samples were prepared by charging (a) and (c) to a 25 ml. round bottom flask and immediately adding the curing agent (b). The ratio of (a) to (b) corresponds to the supplier's recommendations and a rubbery potting compound resulted. After 24 hours curing time, 10 ml of n-butylamine was added, and solubilization was assisted by placing the sample on an automatic shaker. The sample was completely dissolved in 12 (RTV 41) to 24 (RTV 60) hours at room temperature. Spore counts were carried out as indicated below:



48 Hour Incubation at 32°C Before Colony Counting

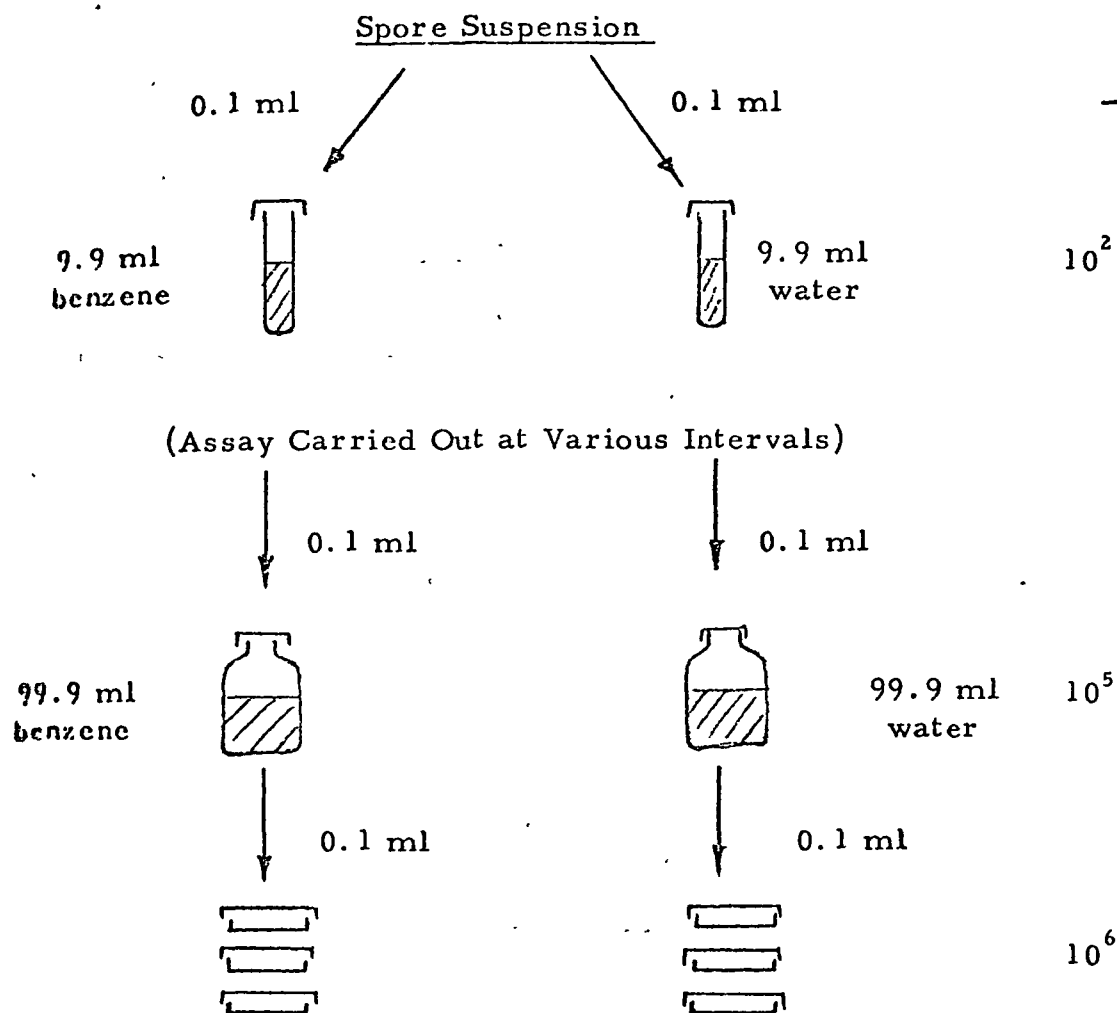
The dilution factor including the inoculation step is 10^5 or 10^6 ; between 10 and 300 colonies were observed per plate at 10^6 dilution. Assays were done in triplicate. Controls in which the same procedure was followed except that spore inoculation was omitted, were all negative, i. e. no colonies were observed.

In the positive control for the experiments described above, silicone prepolymer and curing agent were omitted, but the amine solvent was included. Water was also used as a diluent for comparison with the results obtained using benzene.



48 Hour Incubation at 32°C Before Colony Counting

The high recoveries observed with the butylamine-benzene system in comparison with the butylamine-water system were unexpected, and therefore a comparison of benzene dilution and water dilution was carried out with butylamine omitted.



48 Hour Incubation at 32°C Before Colony Counting

VIII. The Solubilization of the Cured Silicone Polymers with Amine Solvents

A. Determining the Degree of Degradation of Silicone Polymer in n-Butylamine by Viscosity Measurements

The determination of the viscosity of silicone polymer solution was carried out using the Cannon-Fenske viscometer, size 50 in a constant temperature bath (45°C). The n-butylamine solution of silicone oil (50% by volume), silicone prepolymer DC 840 (78.50 g/l)

cured silicone resin DC 840 (78.50 g/l) were prepared. The efflux time was measured immediately after the solution was made and at various time intervals.

ii. Preparation of Silicone (DC 840)-p-Nitrophenol Adduct

Apparatus: A 100 ml 2 neck flask was equipped with a N_2 inlet, thermometer, magnetic stirrer and oil bath.

Procedure: p-Nitrophenol was purified by sublimation at $100^\circ C$, 0.2 mm vacuum. Tetra-butylammonium p-nitrophenoxide was prepared as follows:

p-Nitrophenol, 10 grams, was dissolved in 20 ml methanol. The solution was titrated with tetrabutylammoniumhydroxide titrant using a glass electrode to detect the equivalence point. The volume of the solution was then reduced to about 10 ml by evaporation of solvent using a rotary aspirator at $40^\circ C$. The solution was then cooled slowly with an ice bath. The crystalline product, tetrabutylammonium p-nitrophenoxide was then separated by filtration. The product was dissolved in ethylacetate again and recrystallized from ethyl acetate and dried in vacuo at $40^\circ - 50^\circ C$.

Three different mixtures were prepared as follows: (1) silicone prepolymer DC 840 (~ 0.5 g) in 2 ml of n-butylamine; (2) silicone prepolymer DC 840 (~ 0.5 g) in 2 ml of toluene; (3) cured silicone polymer DC 840 (~ 0.5 g) in 2 ml of n-butylamine. Each mixture was then charged into the flask at room temperature under N_2 atmosphere.

When most of the DC 840 was dissolved, the flask was placed in an oil bath. After complete dissolution, 15 ml of toluene was added to the solution. Then p-nitrophenol (1.0 g) or tetrabutylammonium p-nitrophenoxide (1.0 g) was added to the solution and the temperature was raised to 85°C for 2 hours with no cooling water in the reflux condenser. The temperature was then raised to 90°C to 110°C and refluxed for another several hours with cooling water. After the completion of reaction the oil bath was removed and 20 ml of diethylether (anhydrous) was added. The solution was then washed three times with 20 ml of ice cold 1% HCl solution, 3 times with 20 ml of ice cold 1% NaOH solution, and finally twice with 20 ml portions of saturated NaCl solution. The volume of the washed solution was measured. One ml of this solution was then diluted in diethylether and the concentration of silicone-p-nitrophenol adduct was determined by UV spectrophotometry. The remainder of the washed solution was dried first in a rotary evaporator and then under high vacuum (0.5 mm Hg) for 3 hours. The dried product (~10 mg) was then diluted in 100 ml of diethylether and the concentration of the adduct was rechecked by UV spectrophotometry. The absorbance (optical density) was used to calculate the concentration of the silicone-p-nitrophenol adduct present in product. According to Bouguer-Beer's law

$$A = \epsilon bc$$

The molar absorptivity of DC 840-p-nitrophenol adduct or the extent

of adduct formation can be calculated from the following equation.

$$\epsilon = A/bc$$

where A = absorbance, (optical density)

ϵ = molar absorptivity or extent of adduct formation

c = concentration of DC 840 (moles/liter)

b = length of the path through the absorbing medium
(one cm)

C. Preparation of Silicone-Methanol Adduct

Solutions of the following compositions were prepared by mixing the siloxane with solvent

1.	DC 200 Fluid	1.0 g
	Diethylamine	1.0 g
2.	D ₄ *	1.0 g
	Diethylamine	1.0 g
3.	DC 840 (prepolymer)	1.0 g
	Diethylamine	1.0 g
4.	DC 840 (cured)	1.0 g
	Diethylamine	1.0 g
5.	DC 200 Fluid	1.0 g
	Methanol	1.0 g
6.	D ₄	1.0 g
	Methanol	1.0 g
7.	DC 840 (prepolymer)	1.0 g
	Methanol	1.0 g

* D₄ is octamethylcyclotetrasiloxane

Each solution was then charged into a glass stoppered 50 ml flask at room temperature. One hour after mixing, 25 ml of anhydrous

methanol was added to each of the sample solutions, and the temperature was increased to 45°C by placing the reaction flasks in the 45°C oven for 50 hours. Each solution was evaporated using the rotary aspirator at 45°C for 30 minutes. Then 10 ml benzene was added, and rotary aspirator was continued for 30 minutes. About 40 mg of each solvent free product was then mixed with 0.4 ml of deuterated chloroform (CDCl_3) for NMR analysis.

The D_4 -methanol adduct, sample 2, was prepared as above, and 25 grams of sample 2 was charged into a 75 ml flask and vacuum distilled at 1.4 mm Hg pressure. A rotating collector was used for easy collection of several fractions of distillate.

D. Base-Catalyzed Siloxane Rearrangement Study at Room Temperature by Polymerizing Octamethyl-Cyclotetrasiloxane (D_4) in Anhydrous Methanol

A solution of 10 ml of D_4 diluted to 20 ml with methanol and containing a small amount of bromothymol blue (soluble in methanol but not in D_4) was prepared. Three ml of this solution was transferred to each of 6 vials (5 ml), which contained (1) only methanol (1.0 ml), (2) n-propylamine (0.05 ml), methanol (0.95 ml), (3) n-propylamine (0.2 ml) methanol (0.8 ml), (4) n-propylamine (0.5 ml), methanol (0.5 ml), (5) n-propylamine (0.8 ml) methanol (0.2 ml), and (6) n-propylamine (1.0 ml). The vials were thoroughly mixed and the time was recorded. After 15 days of observation no dye-free phase formed, indicating that the n-propylamine does not catalyze the polymerization of D_4 .

A second solution was prepared containing 10 ml of D_4 diluted to 20 ml with methanol containing a small amount of bromothymol blue and 2×10^{-3} moles of KOH. Immediately after dilution, 3 ml of solution was again transferred to each of 4 vials (5 ml), containing (1) methanol (1.0 ml), (2) n-propylamine (0.05 ml) methanol (0.95 ml), (3) n-propylamine (0.5 ml) methanol (0.5 ml), (4) n-propylamine (1.0 ml). Approximately 10 minutes after the vials were thoroughly mixed, a dye-free phase appeared in the bottom of the vial (1), which contained no n-propylamine. About 15 minutes elapsed before a separate phase was seen in vial (2), about 400 minutes for vial (3), and about 1,500 minutes for vial (4). The volume of dye-free phase increased to 1.3 ml in about 2 hours in vial (1), the same volume formed in vial (2) in about 3 hours, a similar volume of the dye-free phase formed in vial (3) in about 15 hours, while about 30 hours were required for vial (4).

E. The Effects of Solvents on the Solubilization of Cured DC 840 Silicone Resin by n-Butylamine

The effects of solvent on the solubilization of cured DC 840 silicone resin by n-butylamine were investigated. An amine-media solution (50% by weight) was prepared and 0.5 grams of cured DC 840 resin was charged to 5 ml of amine-media solution and solubilization of the cured resin was studied.

IX. Physical Testing of Silicone Polymers (Silastic J, RTV 41 and DC 840)

A. Tensile Strength and Percent Elongation

The tensile strength and percent elongation of Silastic J, both original and reclaimed were determined by the Instron with 90 psi pneumatic jaws and the 200 psi cell and with the digital integrator. The tensile strength (T_f) and percent elongation at fail (E_f) were calculated as follows:

$$T_f = \frac{\text{max. load at fail point}}{\text{cross sectional area}}$$

$$E_f = \frac{\text{length in inches of the sample between marks at fail} - 1}{1 \text{ inch}} \times 100$$

B. Degree of Crosslink

Weighed amounts of the cured, free film samples of silicone resin, both original and reclaimed, were extracted for 48 hours by acetone using a Soxhlet extractor with a coarse grade glass thimble. After extraction, the sample film was vacuum dried at 100°C for 200 hours. The sample was then weighed and the percent of crosslink was calculated as follows:

$$\% \text{ crosslink} = \frac{\text{sample weight after extraction}}{\text{sample weight before extraction}} \times 100$$

C. Hardness Test

The hardness of the dry film of DC 840, both original and reclaimed, were cast on a glass plate and was measured by a Sward Rocker which

calibrated for 50 rocks on the glass plate. The number of rocks is expressed as a percent of hardness shown on glass by dividing by 50 and multiplying by 100.

D. Film Thickness Measurement

The film thickness on steel panels was determined with a GE thickness gauge.

E. Impact Resistance Test

The impact resistance of the DC 840 films on steel panels were determined by the impact tester. The minimum load which caused cracking in the film was taken as the reading in inches-pounds.

F. Chemical and Solvent Resistance Tests

The DC 840 silicone resin, both original and reclaimed, films were cast on steel panels and dried for 10 days. The control panel, prepolymer of DC 840 was baked at 240°C for 1 hour. A few drops of the solvent or chemical was placed on the films and covered with an inverted watch glass. At the end of the test period, about 10 hours, the drops were washed off with water and the film visually examined for evidence of film failure. Resistance to the following chemicals and solvents was checked: 5% H_2SO_4 , 5% NaOH , 10% HOAc , xylene, isopropanol and methyl ethyl ketone (MEK).

G. Thermodegradation Test

The weighed free films (approx. 1 gram) of the DC 840, RTV 41, and Silastic J samples were heated at 300°C. The sample films were

then withdrawn at different time intervals. Each film sample was then placed in the desiccator while cooling to room temperature. Then each sample was weighed and the percent weight lost was calculated as follows:

$$\% \text{ weight lost} = \frac{\text{weight before heating} - \text{weight after heating}}{\text{weight before heating}} \times 100$$

H. Flexibility

The films of reclaimed DC 840 silicone resin were cast on steel panels and dried for 10 days. The control panel, prepolymer of DC 840 film was baked at 240°C for 1 hour. The panels were then bent on a 1 inch conical mandrel and the extent of cracking observed was taken as a measure of the flexibility of the film.

RESULTS AND DISCUSSION

I. Structure of Silicone Polymers

In order to develop a better understanding of the solvent degradation and viability results, it was desirable to have a reasonably detailed knowledge of the structure of the silicone polymers used in this study. Therefore, determinations were made, primarily by spectroscopic methods, of the structure, the phenyl to methyl ratio, the -OH content, the alkyl to silicon ratio, and the molecular weight. The results are presented in the Appendix.

II. Physical Degradation of Cured Silicone Polymers

A. Determination of Solubility Parameter for Cured Silicone Polymers

Burrell's solvent spectrum method (66) as well as Rheineck and Heskin's approach (28) was used to determine the solubility parameter ranges of the cured silicone polymers. A series of purified solvents of increasing solubility parameters in each class of hydrogen bonding was prepared. The results of this experiment are shown in Table II. These results indicate that a complete dissolution of the cured silicone polymer was not achieved in any of the solvents listed. Therefore, the degree of swelling of the cured silicone resins was also determined by a similar technique. The results are shown in Figure VI and Table II. The following conclusions are suggested:

Figure VI. Percent of Swelling of Cured DC 840 and Silastic J in Various Solvents

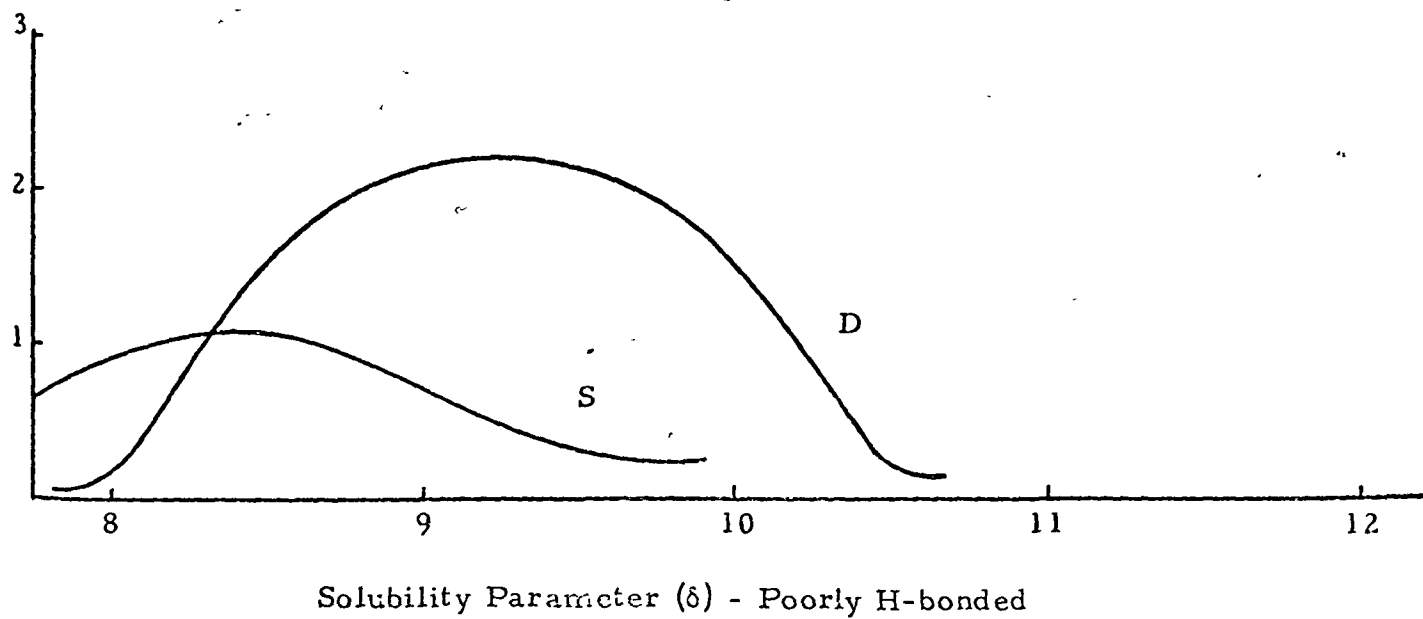
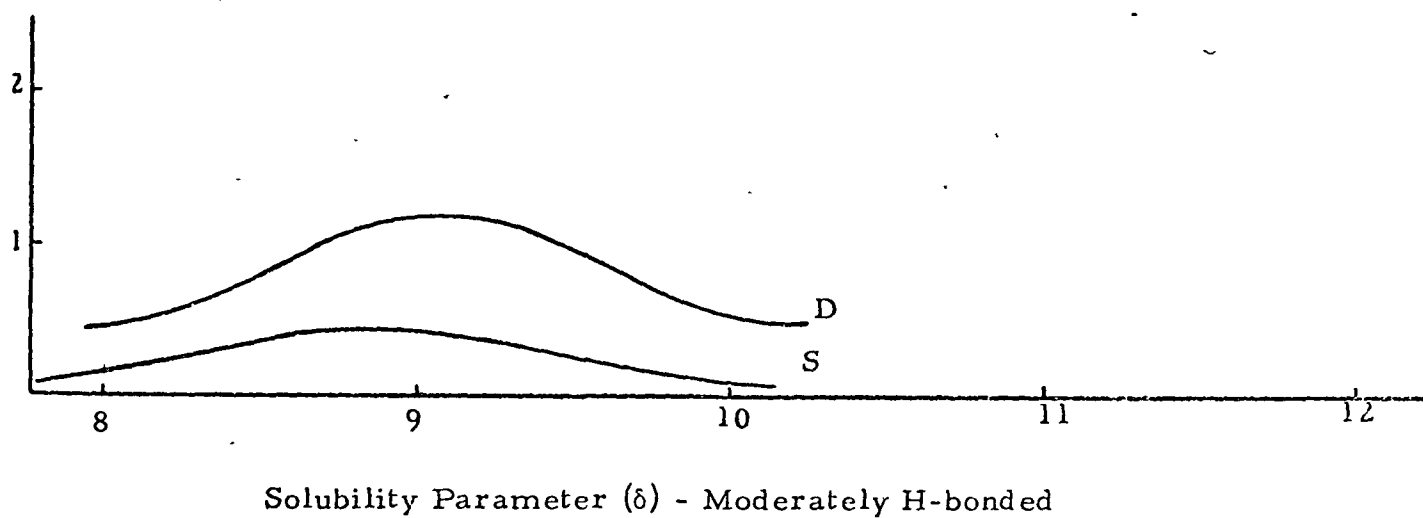
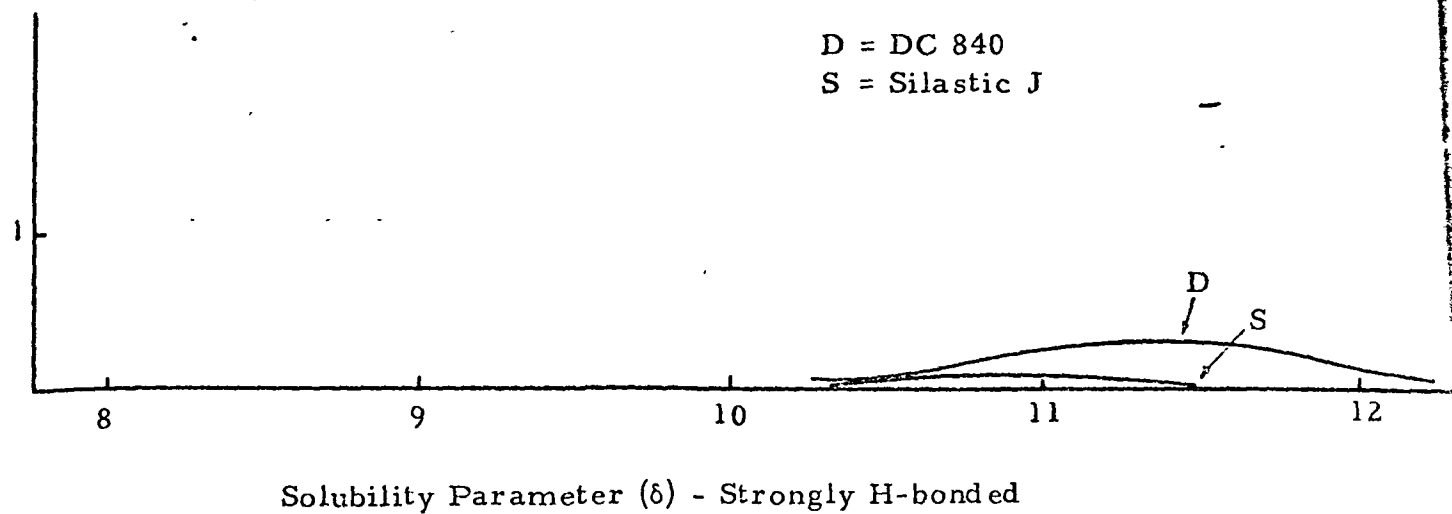


Table II. Solubility Data of Cured Silicone Polymer DC 840

The mixtures of DC 840 and solvent were agitated at 60°C for 48 hrs.

Solvent	Sol. Parameter	Solubility at 60°C
(Class I)		
Hexane	7.3	insoluble
Heptane	7.4	insoluble
Mineral Spirits	7.6	insoluble
Varsol No. 2	8.1	insoluble
Turpentine	8.1	insoluble
Benzonitrile	8.4	insoluble
Dipentene	8.5	insoluble
Carbon Tet	8.6	insoluble
P-Chloro Toluene	8.6	insoluble
Toluene	8.9	insoluble
Benzene	9.2	insoluble
Trichloroethane	9.3	insoluble
Chlorobenzene	9.5	insoluble
Tetralin	9.5	insoluble
1,1,2-Trichloroethane	9.6	insoluble
Tetrachloroethane	9.7	insoluble
Ethylene Dichloride	9.8	insoluble
2-Nitro Propane	9.9	insoluble
Nitrobenzene	10.0	insoluble
1-Nitro Propane	10.3	insoluble
Acrylonitrile	10.5	insoluble
(Class II)		
Ethyl Benzoate	8.2	insoluble
Sec-Amyl Acetate	8.3	insoluble
Methyl Isobutyl Ketone	8.4	insoluble
Methyl n-Amyl Ketone	8.5	insoluble
Carbitol Acetate	8.5	insoluble
Ethyl Acrylate	8.6	insoluble
Cellosolve Acetate	8.7	insoluble
Butyl Acrylate	8.8	insoluble
Diethyl Ketone	8.8	insoluble
Butyl Cellosolve	8.9	insoluble
Ethyl Acetate	9.1	insoluble

Table II. (continued)

Solvent	Sol. Parameter	Solubility at 60°C
Tetrahydrofuran	9.1	insoluble
Diacetone Alcohol	9.2	insoluble
Methyl Ethyl Ketone	9.3	insoluble
Methyl Acetate	9.6	insoluble
p-Dioxane	9.9	insoluble
Acetone	10.0	insoluble
Methyl Benzoate	10.5	insoluble
Methyl Cellosolve	10.8	insoluble
Aniline	11.8	insoluble
Dimethyl Sulfoxide	12.0	insoluble
Dimethyl Formamide	12.1	insoluble
Dimethyl Phosphite	12.5	insoluble
Carbitol	9.6	insoluble
n-Octyl Alcohol	10.3	insoluble
t-Butyl Alcohol	10.6	insoluble
n-Amyl alcohol	10.9	insoluble
n-Butyl Alcohol	11.4	insoluble
Isopropyl Alcohol	11.5	insoluble
n-Propyl Alcohol	11.9	insoluble
Diethylene Glycol	12.1	insoluble

(1) The percent of swelling decreased with an increase of H-bonding strength. This appears to be due to the nonpolar nature of the alkyl radical shielding the somewhat more ionic silicon oxygen backbone of silicone polymers.

(2) The solubility parameter range for good swelling is as follows:

	<u>DC 840</u>	<u>Silastic J</u>
Class I (Poorly H-bonded)	8.8 - 9.8	8.0 - 8.8
Class II (Moderately H-bonded)	8.8 - 9.5	8.5 - 9.2
Class III (Strongly H-bonded)	11.0 - 12.0	10.6 - 11.0

These solubility parameter ranges agree well with the solubility parameter ranges of the prepolymer (DC 840).

(3) Silicone resin, DC 840 gave a higher percent swelling than Silastic J even though the latter has fewer crosslinks. This may be due to the lower proportion of alkyl radical present in the DC 840 resin. In other words, the more highly crosslinked DC 840 has fewer alkyl radicals; thus it is more easily invaded by organic solvents. Another reason is that Silastic J has pigmentation. These factors contributed to the lower percent of swelling.

B. Mechanical Degradation of Swollen Cured Polymer Samples

The mechanical degradation of swollen cured polymer samples was accomplished through the use of high speed blenders and through the use of mortar and pestle in the presence of a large excess amount

of solvent. The high speed blender seems to give better results than mortar and pestle, especially for silicone rubber. The rubbery character of swollen silicone rubber is harder to degrade by mortar and pestle. However, the swollen cured DC 840 is very easily degraded by mechanical force, and this may be a good method for recovery of buried spores as mentioned in the Method of Approach Section. Mechanical degradation of the swollen silicone polymer can be achieved with less severe grinding than is required for the dry polymers. This will minimize the damage to the spores during the degradation process. However, the cured silicone rubbers, such as Silastic J or RTV 41 and 60 are comparatively harder to degrade by this method.

III. Chemical Degradation of Cured Silicone Polymers

As mentioned in the literature review, cleavage of silicone-oxygen bonds always proceeds either by nucleophilic attack on silicon or electrophilic attack on oxygen. In this study an attempt was made to find a non-toxic or low toxicity nucleophilic reagent capable of degrading the cured silicone polymer under the temperatures and pressure limitations imposed. Because a nucleophile attacks by using a pair of its own electrons, the most effective nucleophile is the one whose attacking atom has the valence electrons most available for coordination. Therefore, it is reasonable that the strongest base

should be the most effective reagent for nucleophilic substitution reactions. However, basicity involves thermodynamic measurements whereas nucleophilic "pushing power" or as it is often called, nucleophilicity, generally involves reaction rates. Basicity also most often refers to coordination with H^+ , whereas nucleophilicity involves coordination to carbon. Therefore, a correspondence between the order of basicities and the order of nucleophilicities among various reagents, although reasonable, is by no means axiomatic. The problem of finding a non-toxic nucleophilic reagent capable of degrading the cured silicone polymers at room temperature and normal atmospheric pressure is more complicated. Nucleophilicity relationships for attack on silicone were not available in the literature. Therefore selection of suitable nucleophilic reagents followed the general guide line of the basicity, and availability of the solvents was also considered. According to the 'Scale of Acidity and Basicity' (81), alkali metal hydroxide ions (pK_a 15.7) and amines (pK_a 10) are among the strongest bases and are easily available reagents. Therefore, cured silicone polymers were mixed with alkali metal hydroxide-methanol solutions or with amine solvents, and degradation of silicone polymers was examined. The results of the chemical degradation of cured silicone polymers by these reagents are shown in Tables III and IV. These data indicate the following conclusions:

Table III. Behavior of DC 640 Cured Silicone Polymer in Aqueous Hydroxide Solutions at Room Temperature

Nucleophilic reagents	Sol. parameter	50 mg of polymer in 2 ml reagent					reagent result
		10 min.	2 hrs.	20 hrs.	34 hrs.	68 hrs.	
Diethylamine	8.0	sw	c. sol				c. sol
Piperidine	8.7	sw	c. sol				c. sol
Ethylamine	10.0	c. sol					c. sol
n-Propylamine		sw	c. sol				c. sol
Iso-Propylamine		sw	p. sol	c. sol			c. sol
n-Butylamine	8.66	sw	c. sol				c. sol
Sec-Butylamine		sw	p. sol	c. sol			c. sol
t-Butylamine		sw	sw	p. sol	p. sol	c. sol	c. sol
Amylamine	8.7	sw	c. sol				c. sol
Formamide		no ef	sl. sw	sl. sw	sl. sw	sl. sw	sl. sw
Dimethylformamide	11.77	no ef	sl. sw	se	sw	sw	sw
Ethylene Diamine	12.35	no ef	sl. sw	sw	sw	sw	sw
1, 3-Diaminopropane	11.71	no ef	sl. sw	sw	e. sw	p. sol	p. sol
1, 2-Diaminopropane	11.04	sw	c. sol				c. sol
Diisopropylamine		no ef	sl. sw	sl. sw	sl. sw	sw	sw
N-Ethylethylene Diamine	12.35	e. sw	c. sol				c. sol
Diethylene Triamine	11.54	no ef	sw	sw	e. sw	p. sol	p. sol
Triethylene Tetramine	11.12	no ef	sl. sw	sw	e. sw	p. sol	p. sol
Tetraethylenepentamine		no ef	sl. sw	sl. sw	sl. sw	sl. sw	sl. sw
Pyridine	9.4	no ef	sl. sw	sl. sw	sw	e. sw	p. sol
N-Methylaniline	7.42	no ef	sl. sw	sl. sw	sl. sw	sl. sw	sl. sw

Table III (continued)

Nucleophilic reagents	Sol. parameter	-	50 mg of polymer in 2 ml reagent					reagent result
			10 min.	2 hrs.	20 hrs.	34 hrs.	68 hrs.	
Triethylamine		no ef	sl. sw	sl. sw	sl. sw	sl. sw	p. sol	
Cesium Hydroxide		no ef	p. deg	p. deg	p. deg	p. deg	c. deg	
Rubidium Hydroxide		no ef	p. deg	p. deg	p. deg	p. deg	c. deg	
Potassium Hydroxide		no ef	p. deg	p. deg	p. deg	p. deg	c. deg	
Sodium Hydroxide		no ef	no ef	no ef	no ef	p. deg	p. deg	
Lithium Hydroxide		no ef	no ef	no ef	p. deg	p. deg	p. deg	

no ef - no effect

sl. sw - slightly swollen

sw - swollen

e. sw - extremely swollen

p. sol - partly soluble

c. sol - completely soluble

p. deg - partly degraded but not dissolved

c. deg - completely degraded but not dissolved

The hydroxides were dissolved in anhydrous methanol (2% by weight - pH 13).

Table IV. Behavior of Silastic J (Cured) Polymer in Amines and Hydroxide Solutions at Room Temperature

Nucleophilic reagents	Sol. parameter	50 mg of polymer in 2 ml reagent					reagent result
		10 min.	2 hrs.	20 hrs.	34 hrs.	68 hrs.	
Diethylamine	8.0	sw	sw	sw	p. sol	c. sol	c. sol
Piperidine	8.7	sw	sw	sw	sw	p. sol	c. sol
Ethylamine	10.0	sw	sw	p. sol	p. sol	c. sol	c. sol
n-Propylamine		sw	sw	p. sol	p. sol	c. sol	c. sol
Iso-Propylamine		sw	sw	sw	p. sol	p. sol	c. sol
n-Butylamine	8.66	sw	sw	p. sol	p. sol	c. sol	c. sol
Sec-Butylamine		sw	sw	sw	sw	p. sol	c. sol
t-Butylamine		sw	sw	sw	sw	p. sol	c. sol
Amylamine	8.7	sw	sw	p. sol	p. sol	p. sol	c. sol
Formamide		no ef	no ef	sl. sw	sl. sw	sl. sw	sw
Dimethylformamide	11.77	no ef	no ef	no. ef	sl. sw	sw	sw
Ethylene Diamine	12.35	no ef	no ef	sl. sw	sw	sw	sw
1, 3-Diaminopropane	11.71	no ef	no ef	sl. sw	sw	sw	p. sol
1, 2-diaminopropane	11.04	no ef	sw	sw	sw	p. sol	c. sol
Diisopropylamine		no ef	no ef	sl. sw	sl. sw	sw	sw
N-Ethylethylene Diamine	12.35	sw	sw	e. sw	sl. sol	sl. sol	c. sol
Diethylene Triamine	11.54	no ef	no ef	sl. sw	sw	sw	e. sw
Triethylene Tetramine	11.12	no ef	no ef	sl. sw	sw	sw	e. sw
Tetraethylenepentamine		no ef	no ef	sl. sw	sl. sw	sl. sw	sw
Pyridine	9.4	no ef	no ef	sl. sw	sl. sw	sl. sw	sl. sw
N-Methylaniline	7.42	no ef	no ef	sl. sw	sl. sw	sl. sw	sl. sw

Table IV (continued)

Nucleophilic reagents	Sol. parameter	50 mg of polymer in 2 ml reagent					reagent result
		10 min.	2 hrs.	20 hrs.	34 hrs.	68 hrs.	
Triethylamine		no ef	no ef	sl. sw	sl. sw	sl. sw	sl. sw
Cesium Hydroxide		no ef	no ef	p. sol	p. sol	p. sol	p. sol
Rubidium Hydroxide		no ef	no ef	p. sol	p. sol	p. sol	p. sol
Potassium Hydroxide		no ef	no ef	p. sol	p. sol	p. sol	p. sol
Sodium Hydroxide		no ef	no ef	no ef	no ef	p. sol	p. sol
Lithium Hydroxide		no ef	no ef	no ef	no ef	p. sol	p. sol

no ef - no effect

sl. sw - slightly swollen

sw - swollen

e. sw - extremely swollen

p. sol - partly soluble

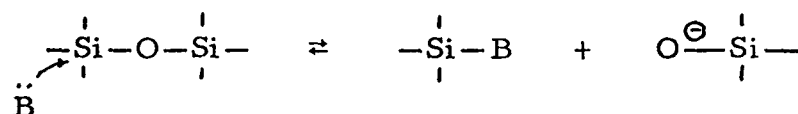
c. sol - completely soluble

p. deg - partly degraded but not dissolved

c. deg - completely degraded but not dissolved

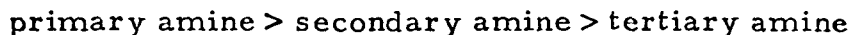
The hydroxides were dissolved in anhydrous methanol (2% by weight - pH 13)

(1) The amine solvents are much better than alkali metal hydroxide-methanol solutions (2% by weight in anhydrous methanol) in degradation of the cured silicone polymers. Hydroxide solutions take about 3 times longer than amine solvents to dissolve the DC 840, and the silicone rubber is not completely degraded at room temperature even after long exposures. This may be due to the equilibrium effect and poor penetration of solvent into the polymer structure. The reaction of base catalyzed degradation is proposed to occur as described in the reaction mechanism study (p.77). The highly reactive silanolate anion

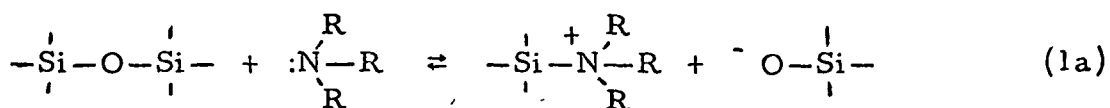


pushes the equilibrium far to the left, therefore, little degradation can be observed. Poor penetration of alkali metal hydroxide solution into the silicone polymer may be attributed to the use of a polar solvent. Alkali metal hydroxides required a polar solvent, such as water or methanol, for a high degree of dissociation. However, highly polar solvents are not good solvents for swelling silicone polymers as the results of the swelling study have shown. Therefore, lower rates of dissolution of silicone polymers, especially the pigmented silicone rubber, are observed. For instance, months are required to dissolve a particle 3 mm in diameter.

(2) The order of decreasing degradation power of amines for silicone polymers is



This difference in order of degradation power (reactivity of amines) can not be explained by inductive effects only. Based on inductive effects, decreasing amine basicity should be tertiary > secondary > primary. This is not the case. As in carbon S_N2 reactions, steric effects are important here, where the differences in basicity are not very great, (pK_{BH^+} of n-propylamine is 10.568, isopropylamine is 10.63) (82), and the nitrogen electrons are sterically shielded from ready access to the silicon atom. Tertiary amines such as triethylamine can not dissolve cured silicone polymer due to high steric hindrance; its nitrogen electrons are sterically shielded from ready access to the silicon atom. However, Doyle and Schenectady (83) reported that gelled organopolysiloxane resin can be dissolved in a trialkylamine. This patented finding seems to contradict the results of this study. A possible explanation for the sharp reduction of degradation power of tertiary amine is not simply the steric effect but may also be attributed to the equilibrium effect resulting from the lack of an active proton for terminating the silanolate anion.



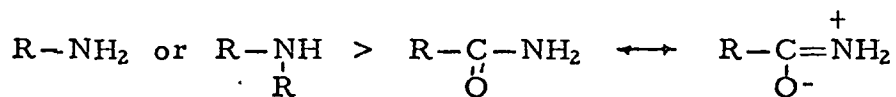
In this reaction, the rate of reverse reaction is very high due to the

high reactivity of the $\text{O}-\overset{\cdot}{\underset{|}{\text{Si}}}-$ and $-\overset{\cdot}{\underset{|}{\text{Si}}}-\overset{+}{\text{N}}(\text{R})_3$; thus driving the reaction to the left. In the presence of moisture, the reaction products of silanolate anion and silylamine cation are terminated by water, forming a comparatively more stable silanol. Hence the reverse reaction of (1a) is reduced and silicone polymer is dissolved in tertiary amine. In Doyle's finding, the gelled organopolysiloxane has a lower degree of crosslinking and most likely contains some moisture which is the product of gellation. (A condensation reaction occurred during storage $2 \text{ } -\overset{\cdot}{\underset{|}{\text{Si}}}-\text{OH} \rightleftharpoons -\overset{\cdot}{\underset{|}{\text{Si}}}-\text{O}-\overset{\cdot}{\underset{|}{\text{Si}}}- + \text{H}_2\text{O}$). Experimental results show that the presence of moisture did facilitate the degradation of silicone polymer in triethylamine.

(3) Diamines or polyamines have very poor dissolution power. This observation is not completely understood. Possibly it is necessary for the solvent to have a hydrocarbon or nonpolar end in order to penetrate the solid polymer. Another possible but less specific reason for their poor dissolution power may be simply the higher polarity of diamines or polyamines. However, the greater solubility in 1,2-diaminopropane compared with 1,3-diaminopropane is not in accord with simple polarity explanation. As previously mentioned in the physical degradation section, high polarity of a solvent retards swelling. Thus, the polar amines will exhibit poorer penetration and reduce the degradation of the polymer. Steric effects will also be important for diamines. Diamines have the functionality required to replace one crosslinkage with

another; however, it does not seem probable that one molecule of diamine would react twice while there is a large excess of unreacted diamine.

(4) Amides cannot degrade the silicone polymer samples. This is because the nitrogen electron pairs are used in conjugative effects within the molecules and are less available for nucleophilic reaction.



The low basicity of amides (such as formamide $\text{pK}_a = 0.48$) reduces the possibility that an amide could be involved in the nucleophilic reaction.

In summary, chemical degradation studies indicate that lower molecular weight (C_3 to C_5) primary and secondary amines are the best chemicals for degradation of cured silicone polymers. Such amines also can easily be evaporated from the silicone polymers which may largely reduce the toxic effect to spores.

IV. Toxicity of Amine Solvents

The viable spore populations in various amine solvents were determined by the plate count technique. The results of the viable spore population in various amines are shown in Tables V and VI. The low colony counts given in Table V indicate that both the amine and heat of mixing are toxic to the spores when using the common plate count procedure. Therefore, a modified procedure was developed to minimize the concentration of the amine present in the plates. A glass rod was

Table V. The Variation in the Incubation Time of the Agar Before Solidification was Mixed with the Nutrient Agar Before Solidification

Amines	Control Count Spores/ml	Time Interval (minutes at room temperature)				
		20	80	160	320	600
		(% of control)				
1, 2-diaminopropane	41 x 10 ⁶	95 x 10 ⁴ (2.3%)	84 x 10 ⁴ (2.0%)	81 x 10 ⁴ (2.0%)	61 x 10 ⁴ (1.5%)	46 x 10 ⁴ (1.2%)
	27 x 10 ⁶	69 x 10 ⁴ (2.3%)	55 x 10 ⁴ (2.2%)	55 x 10 ⁴ (2.0%)	36 x 10 ⁴ (1.9%)	26 x 10 ⁴ (1.0%)
n-butylamine	70 x 10 ⁵	21 x 10 ⁴ (3.0%)	14 x 10 ⁴ (2.0%)	13 x 10 ⁴ (1.9%)	8 x 10 ⁴ (1.2%)	
	59 x 10 ⁵	25 x 10 ⁴ (4.2%)	24 x 10 ⁴ (4.1%)	24 x 10 ⁴ (4.1%)	22 x 10 ⁴ (3.7%)	
piperidine	62 x 10 ⁶	48 x 10 ⁵ (7.7%)	44 x 10 ⁵ (7.1%)	39 x 10 ⁵ (6.3%)	25 x 10 ⁵ (4.0%)	4 x 10 ⁵ (0.65%)
	59 x 10 ⁵	47 x 10 ⁴ (8.0%)	46 x 10 ⁴ (7.8%)	44 x 10 ⁴ (7.5%)	20 x 10 ⁴ (3.4%)	
diethylamine	41 x 10 ⁶	204 x 10 ⁴ (5.0%)	188 x 10 ⁴ (4.6%)	164 x 10 ⁴ (4.0%)	152 x 10 ⁴ (3.8%)	84 x 10 ⁴ (2.0%)
	27 x 10 ⁶	120 x 10 ⁴ (4.4%)	110 x 10 ⁴ (4.1%)	108 x 10 ⁴ (4.1%)	80 x 10 ⁴ (3.0%)	
N-ethyl ethylenediamine	41 x 10 ⁶	360 x 10 ⁴ (8.8%)	354 x 10 ⁴ (8.6%)	356 x 10 ⁴ (8.5%)	350 x 10 ⁴ (8.5%)	320 x 10 ⁴ (7.8%)
	28 x 10 ⁶	220 x 10 ⁴ (8.1%)	200 x 10 ⁴ (7.4%)	190 x 10 ⁴ (7.0%)	160 x 10 ⁴ (6.0%)	130 x 10 ⁴ (4.8%)

Table V. (continued)

Amines	Control Count	Time Interval (minutes at room temperature)					
		20	80	160	320	600	
	Spores/ml		(% of control)				
n-amylamine	59×10^5	30×10^4 (5.1%)	28×10^4 (4.7%)	25×10^4 (4.2%)	12×10^4 (2.1%)	12×10^4 (2.1%)	
						1440	

1. The plates were prepared by mixing one ml of the appropriate dilution with tempered nutrient agar with gentle swirling before solidification.

2. Spore suspension was diluted with amine without cooling.

Table VI. The Viable Spore Population in Vacuum Ampoules 20 hours after the time was spread over the Solidified Nutrient Agar

Amines	Control spores/ml	Time Interval (minutes)				
		20	80	160	320	600
		(% of control)				
pyrrolidine	154×10^5	51×10^5 (33.4%)	31×10^5 (20.1%)	4.5×10^5 (2.92%)	1.0×10^5 (0.65%)	
1,2-diaminopropane	154×10^5	18.3×10^5 (11.9%)	13.3×10^5 (8.6%)	9.0×10^5 (5.8%)	4.8×10^5 (2.5%)	3.6×10^5 (2.3%)
n-butylamine	154×10^5	56.3×10^5 (36.5%)	54.2×10^5 (35.2%)	54.1×10^5 (35.2%)	45.0×10^5 (29.2%)	33.5×10^5 (21.9%)
N-ethylethylene diamine	154×10^5	89×10^5 (57.8%)	60.5×10^5 (39.3%)	57.0×10^5 (37.0%)	57.0×10^5 (37.0%)	35.5×10^5 (23.1%)
piperidine	154×10^5	70.5×10^5 (45.7%)	54.5×10^5 (35.3%)	47.5×10^5 (30.8%)	45.0×10^5 (29.2%)	33.5×10^5 (21.7%)
diethylamine	154×10^5	126×10^5 (81.8%)	84×10^5 (54.5%)	84×10^5 (54.5%)	71.5×10^5 (46.4%)	48×10^5 (31.3%)
DC 840 (cured) 1 gram in 9 ml piperidine	154×10^5	126×10^5 (82.3%)	94.5×10^5 (61.3%)	87.0×10^5 (56.5%)	77.5×10^5 (50.3%)	63.5×10^5 (41.2%)
						35.5×10^5 (23.1%)

1. The plates were prepared by placing 1 ml of the appropriate dilutions on standard medium plates (solidified) and spreading the dilutions over the surface by a glass rod.

2. Spore suspension was diluted with amine in a cold water bath to facilitate the dispersion of heat.

used to spread the spore dilution over the surface of the solidified nutrient agar in the plate. This method will allow the harmful amine solvent to evaporate and hence reduce the concentration of amine. The heat created by the mixing of the spore suspension with amine solvent is dissipated by placing the mixture in a cold water bath. The results of this modified method are shown in Table VI. These results suggest that the toxic effect of the amine is sharply reduced and that amine solvents may be used in the recovery of spores buried within the cured silicone polymers.

V. Spore Recovery Studies on the Silicone Potting Compounds (RTV 41, RTV 60)

Viability studies of spores in cured silicone potting compounds required the use of an organic solvent for the dilution step since it was not possible to dilute the butylamine-silicone rubber solution with water because the silicone precipitated. Cured silicone rubber was dissolved in n-butylamine and recovery of the spores was determined by the plate count technique with the serial dilutions done in benzene. Benzene was selected because it has been reported to be less toxic to spores than many other organic solvents (84) and because it is a good solvent for the silicone rubbers. The use of benzene for serial dilutions necessitated control experiments in the absence of silicone rubber or curing agents. The results of spore viability studies on (1) exposure to n-butylamine followed by dilution with water or benzene, (2) exposure to water followed by dilution with water, and (3) exposure to benzene followed,

by dilution with benzene are presented in Table VII. The data are plotted in Figure VII as log of mean spore counts versus days of exposure. The numbers in the table and the points on the graph represent the mean of colony counts from 20 plates, derived from 4 replicates of 5 samples. The most striking feature of this experiment is the surprisingly high recovery of viable spores on prolonged exposure to n-butylamine followed by dilution with benzene.

The results of studies on spore recovery from inoculated silicone potting compounds RTV 41 and 60 following curing, dissolution in n-butylamine, and serial dilution with benzene are presented in Tables VIII and IX. Recoveries are very high indicating that neither the silicone prepolymer nor the curing agent are sporicidal. Furthermore, it can be concluded that the curing process is not sufficiently exothermic to reduce spore viability. Of course, the small size of the sample would tend to minimize the temperature increase. Comparison with the control in which silicone rubber is omitted (Tables X and VII) shows that there is essentially no reduction in viability caused by the silicone rubber components or the curing reaction. One of the most surprising observations was that the spore population of the ethanol stock suspension was found to be 1.6×10^8 /ml from water dilution runs while values of about 2.5×10^8 to 2.8×10^8 /ml were obtained from the system containing silicone rubber, butylamine, and benzene (Tables VIII, IX) or from the system containing butylamine and benzene (Tables X, VII). If the spore population were based on the water dilution results, recoveries exceeding 100% would be indicated. It is difficult to understand why treatment of spores with butylamine followed by benzene dilution should yield higher colony counts than water dilution results.

Diluent.

Exposed to n-butylamine and diluted
with benzene

Exposed to water and diluted with
water

Exposed to n-butylamine and diluted
with water

Exposed to benzene and diluted with
benzene

0 2 4 6 8 10

Table VII. Colony Counts of Bacillus subtilis Spores after Exposure to Solvents and Diluents for Varying Periods

Days	Treat- ment	Exposed to <u>n</u> -butylamine and diluted with		Exposed to water and dil.	Exposed to benzene and dil.
		benzene	water	with water	with benzene
0		205.0 (2.3118)**	94.20 (1.9714)	147.17 (2.1679)	12.83 (1.1082)
1		251.95 (2.4010)	45.30 (1.6561)	84.50 (1.9269)	10.33 (1.0139)
2		252.40 (2.4021)	45.20 (1.6551)	60.75 (1.7836)	12.50 (1.0969)
3		252.40 (1.4021)	31.45 (1.4976)	50.75 (1.6996)	6.83 (0.7641)
4		217.75 (2.3375)	23.65 (1.3738)	37.83 (1.5777)	3.03 (0.4886)
5		202.25 (2.3060)	32.05 (1.5058)		
6		213.10 (2.3286)	13.80 (1.1399)		
7		193.15 (2.2860)	10.95 (1.0039)		

* Means of the number of colonies counted on 20 plates (five samples, each sample replicated four times.)

** Common logarithm of the means of the number of colony counted.

Table VIII. Colony Counts Obtained from Butylamine Solution of Inoculated Silicone Potting Compound, RTV 41, Using Serial Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies			Average
I	2 days	262	290	270	276
	3 days	286	269	256	271
	4 days	268	228	251	249
	7 days	288	285	234	269
	11 days	245	280	213	246
	16 days	228	233	236	232
	17 days	281	219	207	236
	20 days	262	232	246	247
	22 days	258	245	250	251
	25 days	237	228	231	232
	48 days	226	202	182	203
II	1.5 days	304	254	260	270
	3 days	268	272	273	271
	7 days	269	251	259	260
	11 days	274	263	262	266
	20 days	248	274	246	256

* Zero time is taken as the instant of addition of butylamine to the inoculated, cured silicone rubber. Samples kept at room temperature.

Table IX. Colony Counts Obtained from n-Butylamine Solution of Inoculated Silicone Potting Compound, RTV 60, Using Serial Dilution in Benzene; Dilution Factor = 10^6

Experiment Number	Time*	Number of Colonies				Average
I	0	288	290	286	278	285.5
	1	327	288	259	283	281.3
	2	264	277	245	251	259.3
	3	256	268	248	261	258.9
	4	267	274	254	248	260.8
	7	245	256	238	251	247.5
	10	276	245	221	242	246.0
II	0	280	281	276	310	286.8
	1	277	265	281	288	278.0
	2	287	284	276	310	289.3
	3	292	287	281	254	278.5
	4	269	286	263	246	266.0
	7	246	255	231	258	247.4
	10	247	257	251	258	253.3
III (control) 0 to 10 no colony was observed						

* days

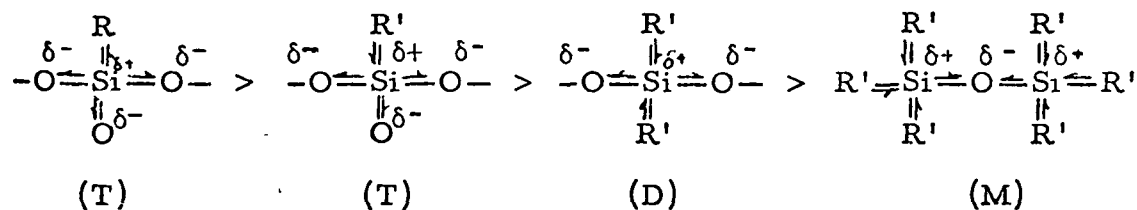
Table X. Colony Counts Obtained after Adding Spore Suspension (0.1 ml) to Butylamine (9.9 ml) in Absence of Silicone Potting Compound Using Serial Dilution in Benzene and in Water; Dilution Factor = 10^6 in Both Cases

Time after mixing* (days)	<u>Number of Colonies</u>					
	Benzene as diluent			Water as diluent		
			(average)			(average)
0	224	251	(238)	102	103	(102)
1	278	289	(283)	101	104	(102)
2	263	282	(272)	97	98	(97)
5	202	206	(204)	82	69	(75)
6	234	244	(239)	13	9	(11)
9	263	212	(238)	14	9	(12)
11	261	238	(249)	15	11	(13)
14	282	264	(273)	12	5	(8)
15	271	272	(271)	10	8	(9)
28	194	194 206	(198)	18 10	9	(16)

*Samples kept at room temperature.

VI. The Mechanism of the Solubilization of the Cured Silicone Polymers with Amine Solvents

The results of viscosity studies on silicone polymers, including silicone oil (DC 200), silicone prepolymer (DC 840) and cured silicone polymer (cured DC 840), are given in Figure VIII and Table XI. The viscosity of the amine-silicone oil solution does not decrease as a function of time, while that of the silicone polymer (DC 840) shows a slight decrease with time. This decreasing trend continues for the first 70 minutes. After this time, constant viscosities were recorded. The cured DC 840 solution also shows decreasing viscosity with time. However, this decrease occurred at a much greater rate than that for the prepolymer. Constant viscosities were observed after 150 minutes. These results indicate that cured resin is degraded and suggest that cleavage occurred primarily at the cross-linking or trifunctional (T) silicone units and not at the linear or difunctional (D) silicone units. Thus, ease of attack by solvent appears to decrease in the order:



where

R = phenyl

R' = methyl

According to Hurd, Osthoff and Corrin (85), difunctional units are more reactive than monofunctional (M) units toward a base. This is

Figure VIII. Variation in Viscosity with Time for a Silicone Oil, a Polysiloxane Prepolymer (DC 840), and a Cured Silicone Resin (cured DC 840) in n-Butylamine Solution. Cannon Viscometer, 50-1711 at 45°C

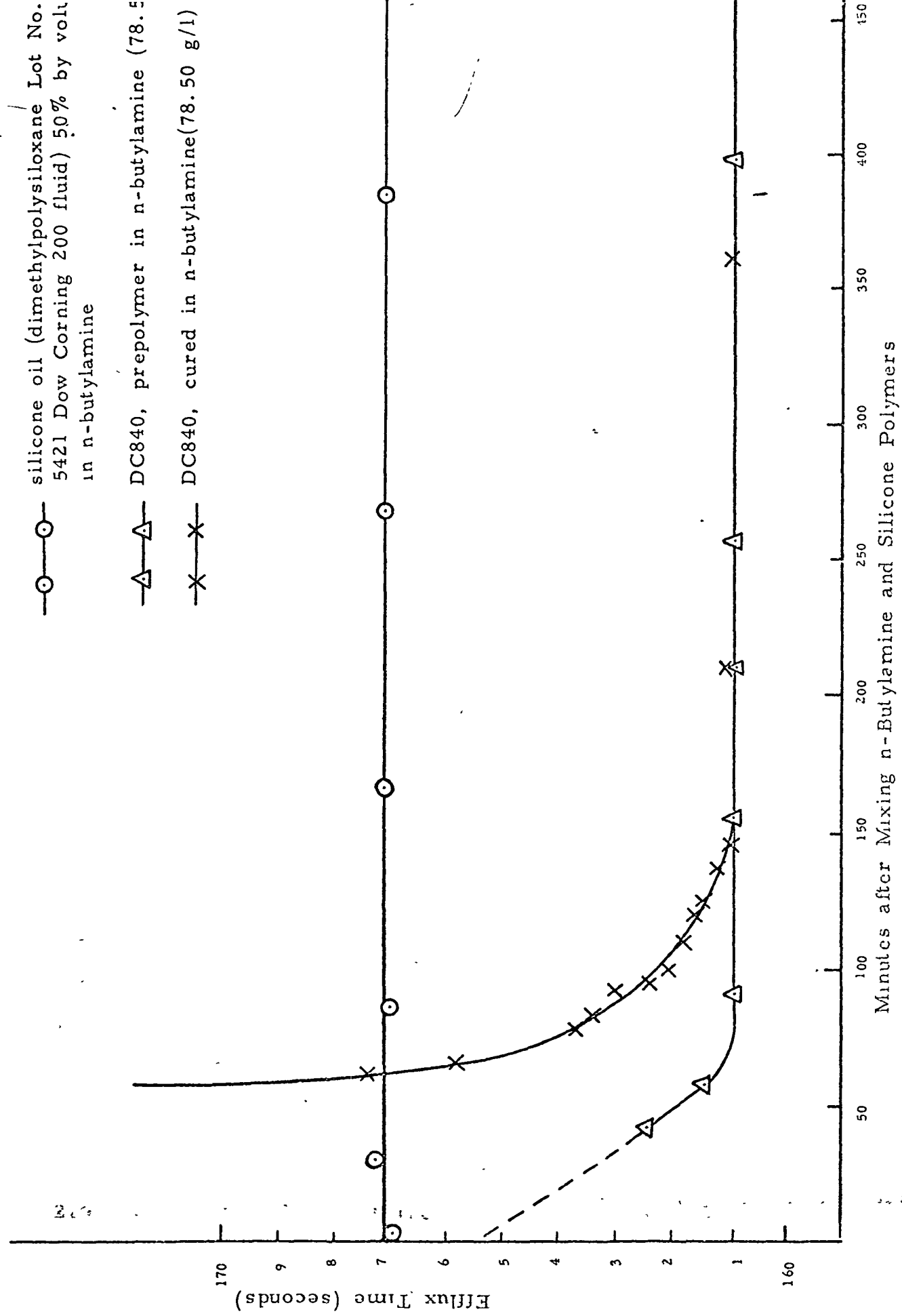
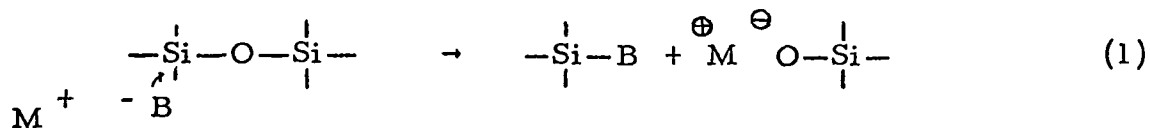


Table XI. Variation in Viscosity with Time for a Silicone
Prepolymer (DC 840) and Cured Silicone Resin
(cured DC 840) in n-Butylamine Solution. Cannon
Viscometer, 50-1711 at 45°C

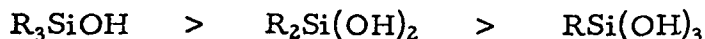
<u>Time (minutes)*</u>	<u>Efflux time (sec)</u>	<u>n²⁵D</u>
<u>Prepolymer</u>		
40	162.5	1.4126
50	161.8	1.4123
60	161.2	1.4103
90	160.9	1.4097
150	161.0	1.4113
210	160.8	1.4103
260	160.9	1.4104
400	161.0	1.4102
480	160.8	1.4103
<u>Cured</u>		
61	167.3	1.4136
66	165.8	1.4134
78	163.7	1.4126
84	163.4	1.4125
92	163.0	1.4126
95	162.4	1.4126
100	162.1	1.4124
110	161.7	1.4129
120	161.5	1.4127
130	161.3	1.4125
140	161.1	1.4115
150	160.9	1.4114
210	161.0	1.4116
360	160.9	1.4114
460	160.9	1.4117

due to the electronegativity of the oxygen atoms which creates a larger positive charge on the silicon atom in a D unit than in an M unit. Therefore a base would be expected to cleave a D-D bond more readily than a M-M bond. They proposed that the attack of a base on a siloxane takes place at the silicone atom with a displacement of the siloxanyl bond



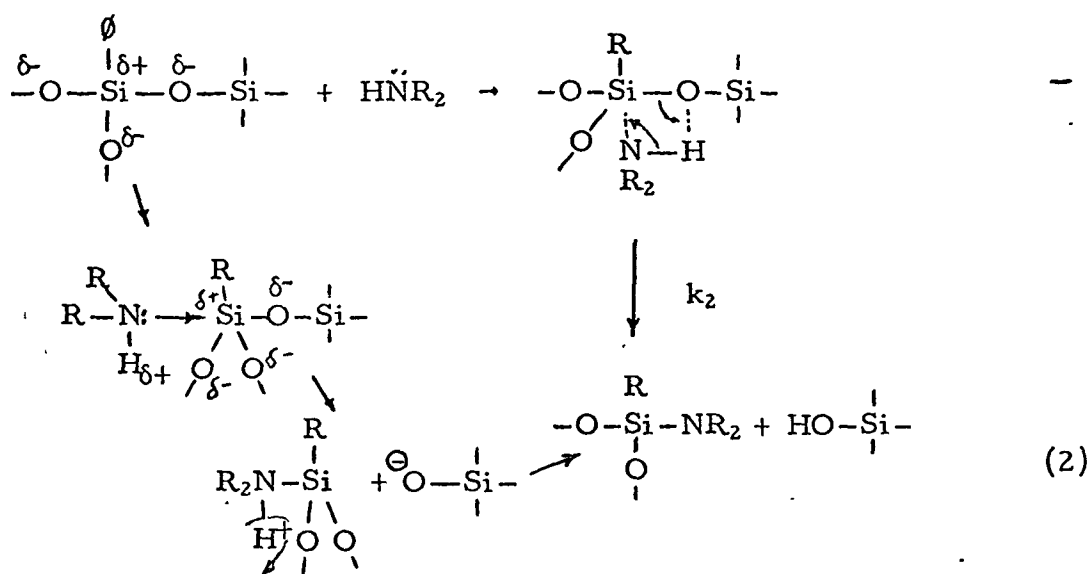
where M = alkali metal B = base

The reactivity of the trifunctional (T) units toward a nucleophile was not obtainable from the literature. Results obtained in this experiment suggest that the trifunctional units are more reactive than D or M units toward nucleophilic substitution. The electronegativity of a third oxygen atom on a T unit is expected to produce a higher partial positive charge on the Si atom than occurs in either the D or M units. This is evidenced by the stability to condensation for the three types of silanols. The stability decreases sharply as the number of hydroxyl groups on a single Si atom increases (86); that is, stability decreases in the order:



Thus, a nucleophilic reagent should cleave a T-T or T-D bond more readily than a D-D or D-M bond. In this study, the nucleophilic reagent, an amine, apparently attacks the Si atoms at T units, rather than at D or M units. Therefore the following reaction mechanism is suggested which may be a "penta-covalent intermediate" (87) or a

conventional displacement reaction



The silicone oil DC Fluid 200 is a linear polymer and its structural units are mostly D units with very few M units; the latter occur only as end groups. It appears very likely that under existing conditions (45°C), the amine functional groups did not cleave the D-D or D-M bond. Therefore the viscosity of DC Fluid 200 was not affected and no degradation was observed. The structural units of the silicone resin DC 840 are largely T units. Some of the alkyl radicals attached to the T unit are phenyl radicals. These phenyl radicals have the tendency to withdraw electrons from the silicon atom, increasing the positive charge on the silicon and enhancing its reactivity toward nucleophilic displacement. Therefore, an amine functional group can readily attack the silicon atom of the T unit at lower temperatures to cleave the T-T or T-D or T-M bonds. The cured DC 840 has a larger proportion of T-T and T-D bonds than the prepolymer due to the condensation which occurs during the curing process. Hence, the cured

DC 840 has a higher initial viscosity and a greater reduction in viscosity than the uncured prepolymer as a result of nucleophilic attack by amine.

The results of this experiment also indicated that during degradation of DC 840, an equilibrium was obtained as shown in Figure VIII. After the equilibrium state was reached the viscosity of the solution remained constant. The fact that the same equilibrium viscosity is obtained from the cured and uncured resins supports the contention that cross-links are preferentially attacked.

Some reports (88-90) in the literature indicated that silylamines are susceptible to attack by various nucleophilic reagents resulting in the cleavage of the silicon-nitrogen bond.

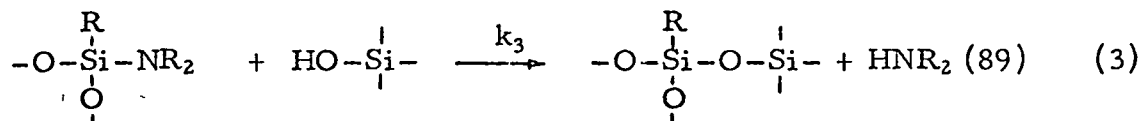


where X may be O, NH, or S

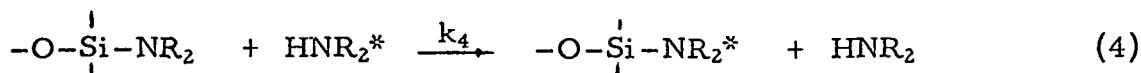
Rochow (88) stated that an $-\text{NH}_2$ group attached to silicon is easily replaced by an $-\text{OH}$ group upon hydrolysis, generating ammonia. Speri (89) studied the reaction of hexamethyldisilazane with alcohols to give aliphatic trimethylsilylethers. Langer et al (90) extended this reaction to prepare a large number of silyl ethers belonging to this class. In each of the above reactions of silylamines or silazanes with H_2O , $\text{R}-\text{NH}_2$, alcohols or a silanol, it appears that a nucleophilic substitution on silicon occurs (90), which results in the formation of a new

$\text{--}\overset{|}{\underset{|}{\text{Si}}}\text{--O--}$, or $\text{--}\overset{|}{\underset{|}{\text{Si}}}\text{--N=}$ linkage.

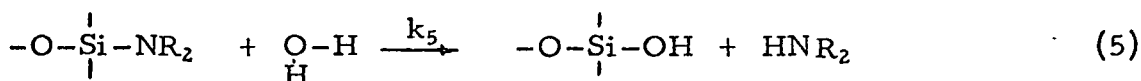
In light of these studies, we may expect that the degradation product of the silylamine or silazanes would have the reverse reaction as follows:



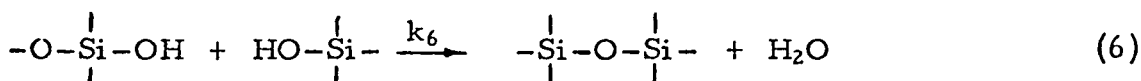
or would react with another amine molecule as:



In the presence of moisture, the silylamine would react with H_2O to form silanol and amine molecules:



The silanols, however, are very prone to condensation of their silanol groups to the siloxane bonds and H_2O , especially with base catalysis provided by amines.



One may summarize the effect of the reactions above during amine-catalyzed degradation and equilibration of cured DC 840 silicone polymer. Reaction (2) causes an decrease in molecular weight of the system; reactions (3) and (6) increase the molecular weight while reaction (4) and (5) produce no change in the number of molecules in the system and therefore, do not affect the molecular weight. Referring to Figure VIII, it would be observed that viscosity decreased rapidly during

the first hour, indicating reaction (2) is proceeding rapidly. This strongly suggests that reaction (2) predominates initially when cross-links are numerous. Rapid formation of silylamine and silanol soon leads to an increase in the rate of (3). When viscosity becomes constant the rate of reaction (2) equals the rate of reactions (3) and (5); thus, the attainment of the final equilibrium. These results agree with those obtained using viscosity measurements.

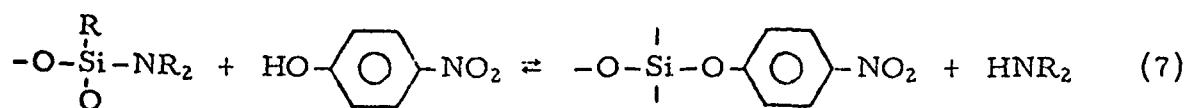
Several experiments were performed in an attempt to isolate or detect the reaction products; that is, silylamine, silazane, and silanol. One method involved fractional distillation of silicone resin-amine solution. Another technique utilized low temperature vacuum evaporation of silicone resin-amine solution followed by elemental analyses, to obtain the percent nitrogen in the sample. Finally IR and NMR spectrophotometric studies of silicone resin-amine solutions were carried out. However, these attempts failed to produce any evidence for the presence of proposed products. This may be due to the low stability of the products to hydrolysis or condensation to reform the siloxane and amine (93, 94, 95).

Pike (93) studied the rates of reaction of triphenyl- and triethylsilanols with a series of silylamines in bis(2-methoxyethyl)ether and reported that the specific reaction rate constants for the condensation of silylamines with silanols were high. Condensation of triphenyl silanol (0.3610 mole/l) with N, N-diethylaminotrimethylsilane $(\text{CH}_3)_3$

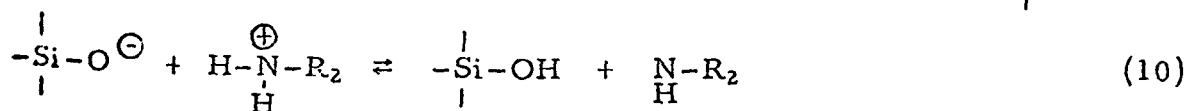
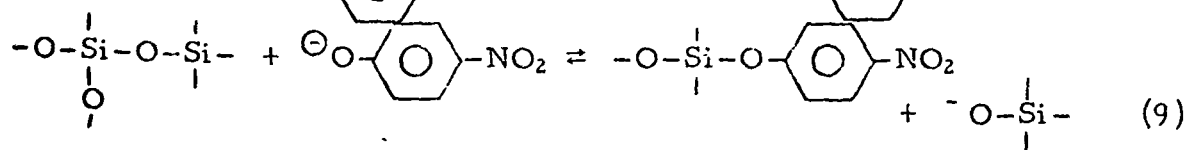
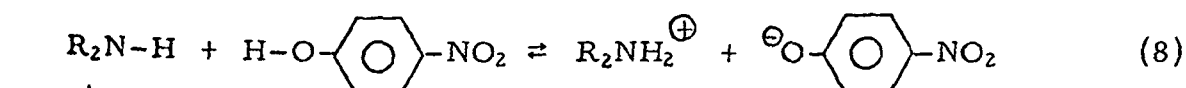
$\text{SiN}(\text{C}_2\text{H}_5)_2$, (0.1715 mole/l) at 40°C has a rate constant of 5.32×10^{-4} mole/l⁻¹ sec⁻¹. As soon as the concentration of amine solvent decreased in the sample solution the equilibration of siloxane shifted to favor the silanol and silylamine which then condensed out. Therefore, fractional distillation or vacuum evaporation of the sample solution failed to show any sign of the presence of silylamine.

The IR and NMR spectrophotometric studies produced no evidence for the existence of reaction products in the sample solution. This is likely due to the fact that the $-\text{Si}-\text{N}=$ peak could not be identified. The problem in deciphering any NMR spectra results from the difficult determination of protons attached to nitrogen atoms, as well as from the lack of information involving nitrogen atom effects on the proton peak of $\text{H}-\text{Si}-\text{N}-$.

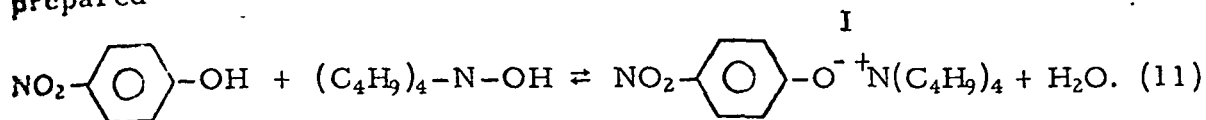
Due to the instability of the degradation products, silylamine and silanol, the preparation of a silicone-p-nitrophenol adduct was carried out to determine whether or not a silylamine is formed during the solubilization reaction of cured silicone polymer by amine solvents. The reaction is expected to be:



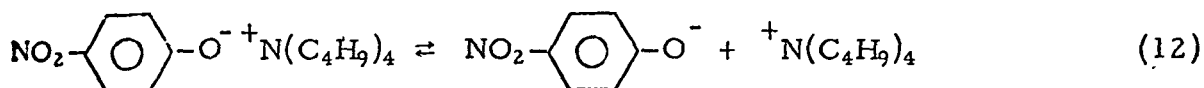
However, there is a possibility that amines could react with p-nitrophenol first, and then the resulting anion might attack the silicone:



In order to investigate the reactivity of p-nitrophenol anion toward silicone polymer, a salt, tetrabutylammonium-p-nitrophenoxide was prepared



Dissociation of the salt (I) formed the anion, and therefore the salt (I)



could be used to trap the silylamine.

The results of using p-nitrophenol to trap the silylamine is shown in Table XII. Results indicate that when amine is present, the concentration of adduct produced in the sample solution is about 7 times higher than that obtained in absence of amine. The data also indicates that there is no significant difference between prepolymer and cured DC 840 in formation adduct.

The results of using tetrabutylammonium-p-nitrophenoxide (TAP) to trap the silylamine are shown in Table XIII. The concentration of adduct in presence of amine is a little lower than the sample solution to which no amine had been added. In Table XIV p-nitrophenol with amine and TAP alone were compared. The data indicate no significant differences between p-nitrophenol and TAP as the trapping reagent. These results suggest that the p-nitrophenol does not react directly with silylamine but reacts with amine to form a p-nitrophenol anion. The anion then attacks silicone polymer, as shown in reactions (8) and

Table XII. Trapping the Silylamine by p-Nitrophenol

Temp. (°C)	Time (min)	molar absorptivity (extent of adduct formation = A/bc)		
		with amine (ϵ_a)	without amine (ϵ_b)	ratio ϵ_a/ϵ_b
<u>DC 840 prepolymer</u>				
90	1220	6,995	998	7.01
110	1280	15,764	2116	7.45
110	1395	16,365	2093	7.82
<u>DC 840 cured</u>				
90	720	4,614		
90	1200	4,800		
100	1100	10,766		
110	1100	18.133		

Table XIII. Trapping the Silylamine by Tetrabutylammonium-p-nitro-phenoxide

Temp (°C)	Time (min)	molar absorptivity (extent of adduct formation = A/bc)		
		with amine (ϵ_a)	without amine (ϵ_b)	ratio ϵ_a/ϵ_b
<u>DC 840 prepolymer</u>				
90	600	475	752	0.6316
90	630	590	919	0.6399
110	600	1270	2015	0.6322

Table XIV. Comparison of Trapping Effectiveness of the Silylamine by p-Nitrophenol and Tetrabutylammonium-p-nitrophenoxide

Temp (0°C)	Time (min)	molar absorptivity (extent of adduct formation = A/bc)		
		with amine (ϵ_a)	without amine (ϵ_b)	ratio $\bar{\epsilon}_a/\epsilon_b$
<u>DC 840 cured</u>				
46	600	167*		
		171*		
<u>DC 840 prepolymer</u>				
95	1200	8261*	8958**	0.9222

* Trapping the silylamine by p-nitrophenol.

** Trapping the silylamine by tetrabutylammonium-p-nitrophenoxide.

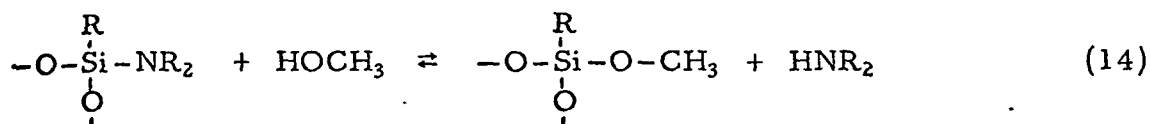
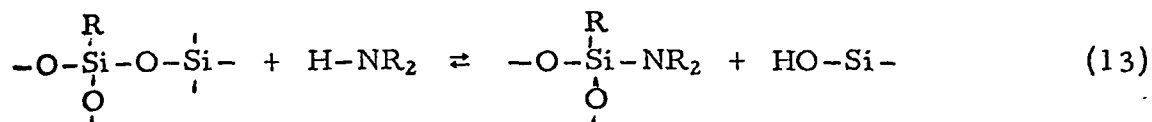
(9). The results in Table XIII can be interpreted in the same manner. Phenolate anion is the attacking reagent, and amine suppresses TAP dissociation. Thus, p-nitrophenoxide adduct formation would be lower in the presence of amine as observed.

Table XV. Trapping the Silylamine by Methanol with NMR Analysis

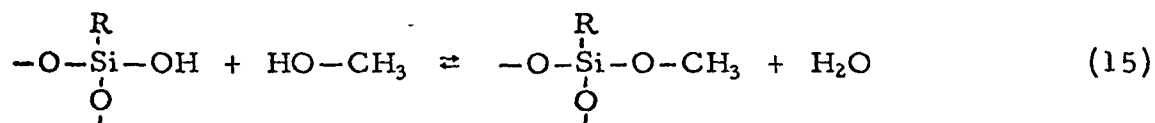
Silicone polymer	NMR peak of Si-O-CH ₃ at δ 3.52	
	<u>no amine present</u>	<u>with amine present</u>
DC 200	no	no
D ₄	no	yes
DC 840 (prepolymer)	no	yes
. 840 (cured)	no	yes

The results of trapping the silylamine by utilization of methanol is shown in Table XV. The methoxy silane peak is identified at δ 3.52 and methanol peak at δ 3.44 (78).

The reaction of trapping silylamine by methanol appears to be



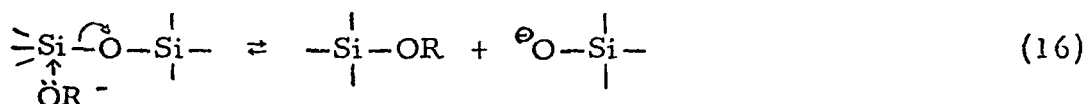
There is a side reaction which may occur. This is a direct condensation of methanol with silanol. However the possibility of this reaction



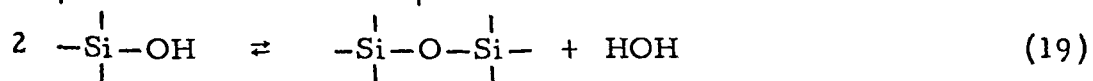
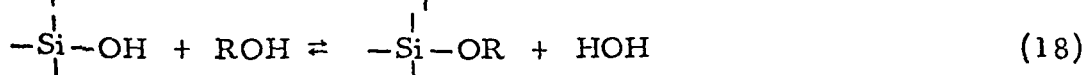
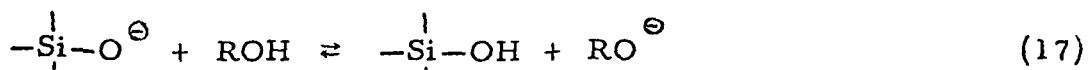
is very low because of higher activation energy required for this condensation. The linear polymer of silicone oil DC 200 has neither silanol functional groups nor silylamine formed during reaction. Therefore, no peak for organomethoxysilane was observed regardless of the presence of amine. With D₄ and DC 840 on the other hand, participation of amine in reaction (13) is an important factor preceding the formation of organomethoxysilane. This may be evidence that reaction (13) occurs during solubilization. Reactant D₄ initially has neither silylamine nor silanol, hence neither reaction (14) nor (15) can occur. However, if reaction (13) occurs due to the presence of amine, the products of either silylamine or silanol can produce reactions (14) and (15) to form methoxysiloxane.

An effort to isolate the methoxysilane by distillation failed. This difficulty in isolating methoxysilane appears to be caused by the very high reactivity of organomethoxysilane, especially when the methoxy group is attached to a T unit. Kuznetsova et al (96) did isolate the trimethylmethoxysilane as an azeotrope with methanol (fraction 49-52°C) by distillation; however, a search of the literature for a report of separation of a methoxysilane which is attached to a trifunctional siloxane was unsuccessful.

Vornokov and Shabarova (97) reported that organoalkoxysilanes were synthesized by cleavage of organosiloxanes with alcohols (primary or secondary containing from 4 to 12 carbon atoms) in the presence of alkaline catalyst. A scheme was proposed by them for the reaction mechanism as follows:

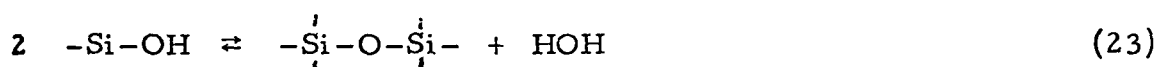
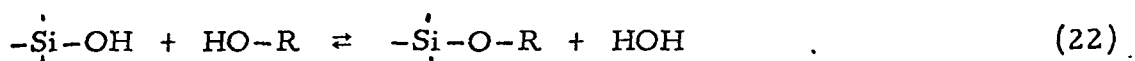
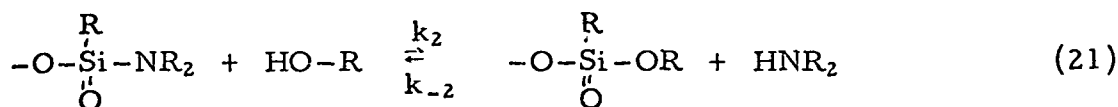
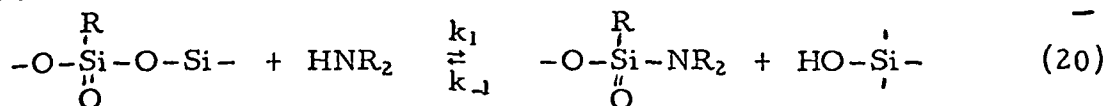


where OR^- is from a hydroxide ($\text{R} = \text{H}$) or an alcoholate of an alkali metal.



Hence, in their experiment water was liberated. Removal of water is essential for syntheses. However no water was collected in our method. The possible reaction of amine catalyzed method may be explained as

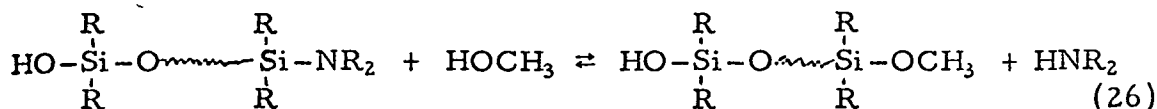
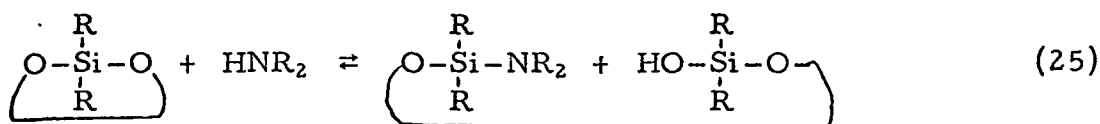
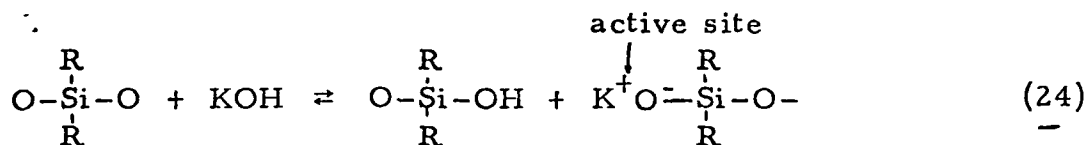
follows:



Amine cleaves the $\underset{|}{\text{Si}}-\text{O}-\underset{|}{\text{Si}}-$ of T units to form silylamine and silanol as in reaction (20). The silylamine then reacts with alcohol by nucleophilic substitution to form organoalkoxysilane and regenerate the amine. The reverse reaction of (20) and forward reaction of (21) are competing reactions. If $k_{-1} < k_2$ and the concentration of $(\text{R}-\text{OH}) > (-\text{Si}-\text{OH})$ then organoalkoxysilane is formed as product. Pike (91) reported that toward the same silylamine n-propanol condensed at a faster rate than triphenyl- or triethylsilanol. Experimentally, the concentration of alcohol is much higher than the concentration of silanol. Therefore, formation of organoalkoxysilane at lower temperatures such as 45°C, is possible. However, reactions (22) and (23) were not possible in this experiment due to the low concentration of silanol and higher activation energy requirement. Therefore, no water was liberated.

Osthoff et al (98) observed that the base-catalyzed siloxane rearrangement process could be studied at room temperature by polymerizing octamethylcyclotetrasiloxane (D_4) with various bases in a

medium of anhydrous methanol or ethanol. The polydimethylsiloxanes of low molecular weight including D_4 are soluble in methanol over a wide range of concentrations. The polydimethylsiloxanes of high molecular weight, however, are not appreciably soluble in methanol, and if a solution of D_4 in methanol is polymerized, the higher molecular weight siloxanes separate as a distinct phase. The separation of the higher molecular weight products as a new phase is useful in comparing the relative effectiveness of different bases to promote the polymerization of D_4 . An attempt to polymerize D_4 in anhydrous methanol utilizing amines as a catalyst failed. After 15 days of observation, no dye-free phase formed, indicating that the n-propylamine does not catalyze the polymerization of D_4 . This might be interpreted as an indication that the ring does not open; however, NMR studies show that organomethoxysilane was formed in the sample solution. This result suggests that amine does attack the silicon atom in D_4 to cleave the siloxane rings to form silylamine and silanol. The silylamine then reacts with methanol to form organomethoxysilane and silanol. Polymerization is not observed because the ring opening reaction does not create an active site as KOH does. In this case it is suggested that silicon atoms bearing only two oxygens react (perhaps slowly) while in the solvent degradation discussion preferential reaction of $\begin{array}{c} \text{O} \\ | \\ -\text{Si}-\text{O} \\ | \\ \text{O} \end{array}$ was stressed. The difference is a matter of relative rates and possibly the participation of methanol during nucleophilic attack by amine.



The influence of amine (at various concentrations) on the KOH catalyzed D₄ polymerization was also investigated. According to the findings of Osthoff (98), the time required for the appearance of the dye-free phase was dependent on both the concentration of D₄ and the concentration of the base in the methanol solution as well as the nature of the base. In this experiment, both the concentration of the base and the concentration of the D₄ in the methanol solution were kept constant. If the n-propylamine did not affect the rate of polymerization, the second phase in the alcoholic polymerization reaction should show up at the same time. However, the results of these experiments show that amine retards the onset of polymerization. The induction period was directly proportional to the concentration of the amine present. n-Butanol also suppressed the onset of polymerization, however, n-pentane and 2-methyl-butane do not retard the rate of polymerization. The possible explanation of this result is that dissociation of silanolate, the reactive site for the polymerization is suppressed by the formation of a comparatively stable complex. Kucera et al (99) call this phenomenon of

deceleration of polymerization on addition of relatively strong bases to a basic active center 'isobasic termination'.

The effects of solvent on the solubilization of cured silicone resin by n-butylamine was investigated. It was found that as the dielectric constant of the solvent was increased by selected solvents (n-butanol, n-propanol, ethanol, methanol, acetonitrile), the equilibrium swelling of the cured silicone resin increased. A 30% solution of acetonitrile in n-butylamine dissolved the cured resin within 48 hours.

In order to test the proposed reaction mechanism, the steric effect of the amine solvent was also studied. The amine-cured silicone resin concentration ratio was kept constant and the speed of dissolution of the cured silicone resins studied. The dissolution power of the various amines are as follows:

(1) n-butylamine > iso-butylamine > sec-butylamine > tert-butylamine

(2) n-propylamine > iso-propylamine

However, the order of the basicity (100) of amines is different from the dissolution power.

(1) n-butylamine (10.64) > sec-butylamine (10.56) > tert-butylamine (10.45) > iso-butylamine (10.42)

(2) iso-propylamine (10.63) > n-propylamine (10.568)

When the attacking group is bulkier, the reaction rate is slower. This result suggests that the reaction is very likely a bimolecular reaction.

VII. Properties of Reclaimed Silicone Rubber and DC 840 Coating

Based on the mechanism for amine solubilization as presented previously (Reaction 3, p.80), it was anticipated that a significant number of crosslinks would reform on evaporation of the amine solvent. In support of this hypothesis, it was determined by an extraction technique as shown in Table XVII that recrosslinking occurred. Regeneration of original crosslinks when amine is removed at room temperature is indicated by the high percentage of reclaimed sample that cannot be extracted. These findings have suggested exciting new possibilities for (1) the recovery of silicone molds and, (2) the silicone coating of heat-sensitive materials. It was hoped that recrosslinking would be accelerated at higher temperatures, but this was not observed as indicated by the 230°C entries in Table XVII. Many competing processes are occurring and as a result it is difficult to explain these high temperature results. The relative rates of removal of amine and water may effect the extent of crosslinking. Reactions of higher activation energy, such as condensation of a silylamine with a second silanol, might occur to a significant extent at higher temperatures. It should be noted that the times allowed for recrosslinking at the higher temperatures are much shorter than at lower temperatures.

One of the greatest difficulties in the use of silicone resins for surface coatings is that long times and high temperatures are required to complete the condensation. Initially, condensation takes place

relatively rapidly, but the reaction then slows down because of steric hindrance (101) and high temperatures and very active catalysts are required to accelerate it. The curing temperatures are limited by the construction of the ovens available in the lacquering industry and the fact that above 250°C in addition to condensation, oxidation of the organic radicals and splitting of the Si-C bonds take place to an increasing extent (101). Many attempts have been made to lower the baking temperature, such as using polysiloxanes containing acyloxy groups (102). However, the cured silicone resin-amine solution system may be a good solution for this curing problem. A report describing these finds has been submitted for patent consideration.

The characteristic properties of room temperature curing silicone coating (reclaimed cured silicone resin DC 840) was also studied. The results are given in Tables XVIII and XIX. The room temperature cured DC 840 silicone coating films appeared clear and glossy, colorless, smooth and free of pin-holes. In comparison with baked control sample films, it was hard to see a difference. The films showed good hardness and excellent chemical resistance but poor solvent resistance, flexibility and impact resistance; the control film has similar properties. The kind of amine solvent and composition of solvent did affect the drying time and the film properties. Solvents such as 1,2-diaminopropane gave a hazy and inferior film. This might be attributed to the fact that diaminopropane has low volatility compared to other

amines and therefore, it does not evaporate readily from the films.

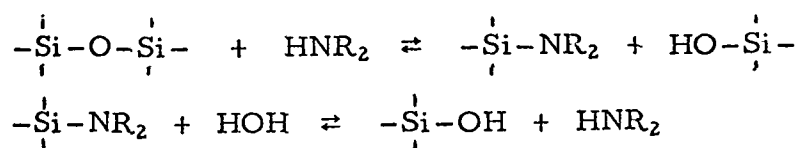
The amine that remains during film formation may be incompatible — and cause hazy and inferior films.

This new room temperature curing silicone resin has a high solids content but low viscosity. It is possible to make the solids content as high as 75% DC 840 while retaining a viscosity of 100-200 centipoises at 25°C. Thus, there is a high possibility of formulating a high solids coatings.

The test panels of the 14 day room temperature cured DC 840 coating and control panel were exposed to UV radiation for a total of 200 hours by means of a National UV Degradation Accelerometer. The accelerometer light source is a G.E. UA-11B Photochemical Corex-filtered mercury quartz lamp. The degree of yellowness resulting from UV exposure was determined by visual inspection of the difference between a control panel and an exposed panel. The results showed excellent UV resistance for both oven cured and room temperature cured DC 840 coating films. However, reclaimed coating films seemed to show more yellowing. This is possibly due to some remaining amine solvent contributing to yellowing.

The properties of reclaimed silicone samples from a silicone mold (Silastic J) were studied. The mold was first dissolved in amine solvent, and then the amine solvent was evaporated at room temperature. The tensile strength and percent elongation of a cured

control sample and a reclaimed sample of Silastic J silicone rubber are given in Table XVI. The results show that reclaimed Silastic J regained about 60% of its tensile strength and about 80% of its percent elongation. These results were obtained after a short period of solution storage; the tensile strength and percent elongation were lower following evaporation after longer storage time. This tendency may be attributed to further degradation of polymer molecules by amine solvent and by the presence of moisture.



Another possible reason is sedimentation of pigment or filler during the storage period. This would result in separation of pigment and polymer and would create an uneven distribution of pigmentation. Therefore, in the reclaiming process, the solution state should be maintained for as short a time as possible to avoid complications.

The thermal stability of the reclaimed sample and control sample of silicone polymer were also studied. The results of these studies are given in Figure IX. These results indicate that the thermal stability of reclaimed samples is somewhat inferior. This may be due to evaporation of residual amine by heat or to some degradation of polymer by residual amine at higher temperatures. An especially high weight loss was noted for reclaimed RTV 41 (as high as 30%). This is more than 3 times higher than the control sample. Reclaimed samples of DC 840 and Silastic J showed excellent heat resistance, however.

Table XVI. Tensile Strength and Percent Elongation of Cured and Reclaimed Dow Corning Silastic J Silicone Rubber

Sample	Tensile strength	% recovered**	% elongation	% recovered
Control sample*	5.07×10^5	100	123	100
Reclaimed sample**				
Cured Silastic J dissolved in n-butylamine for				
5 days	2.89×10^5	57.01	103	83.74
10 days	2.49×10^5	49.12	88	71.54
60 days	1.47×10^5	28.94	78	63.41

* Control sample was prepared as recommended by manufacturer.

** Reclaimed samples were prepared by dissolving the control sample in n-butylamine, retaining in solution for the specified number of days, and then preparing the sample specimen by evaporation of amine at room temperature for 10 days.

*** % recovered = reclaimed sample/control sample.

Table XVII. The Degree of Crosslinking of Cured and Reclaimed DC 840 by Solvent Extraction Method

<u>Sample</u>	<u>% Nonextractable</u>	<u>% Nonextractability recovered</u>
Control sample*	86.5	100
Reclaimed sample**		
1) dried at room temp. for 48 hrs	66.6	76.99
2) baked at 60°C for 24 hrs	65.2	75.38
3) baked at 100°C for 2 hrs	77.3	89.36
4) baked at 230°C for 5 min	5.8	6.68
5) baked at 230°C for 10 min	19.3	22.36
6) baked at 230°C for 15 min	25.7	29.71
7) baked at 230°C for 20 min	29.9	34.45

* Control sample was cured at 240°C for 1 hour.

** Reclaimed sample prepared by dissolving control sample in n-butylamine; then the samples were air dried or baked.

Silicone resin	Time at Failure (10 hours spot test)					
	5% NaOH (hour)	5% H ₂ SO ₄ (hour)	10% HOAc (hour)	Xylene (min)	Isopropanol (min)	MEK (min)
DC 840						
Control (prepolymer baked at 240°C for 1 hour)	10	10	10	1	95	1
Cured DC 840 dissolved in 1, 2-diaminopropane	5	6	5	1	45	1
Cured DC 840 dissolved in n-amylamine n-propylamine (4:1)	10	10	10	1	95	1
Cured DC 840 dissolved in diethylamine	10	10	10	1	95	1

* Control sample was baked at 240°C for 60 minutes. The other three samples were not baked but air dried for 10 days.

** One mil dry films on glass plates.

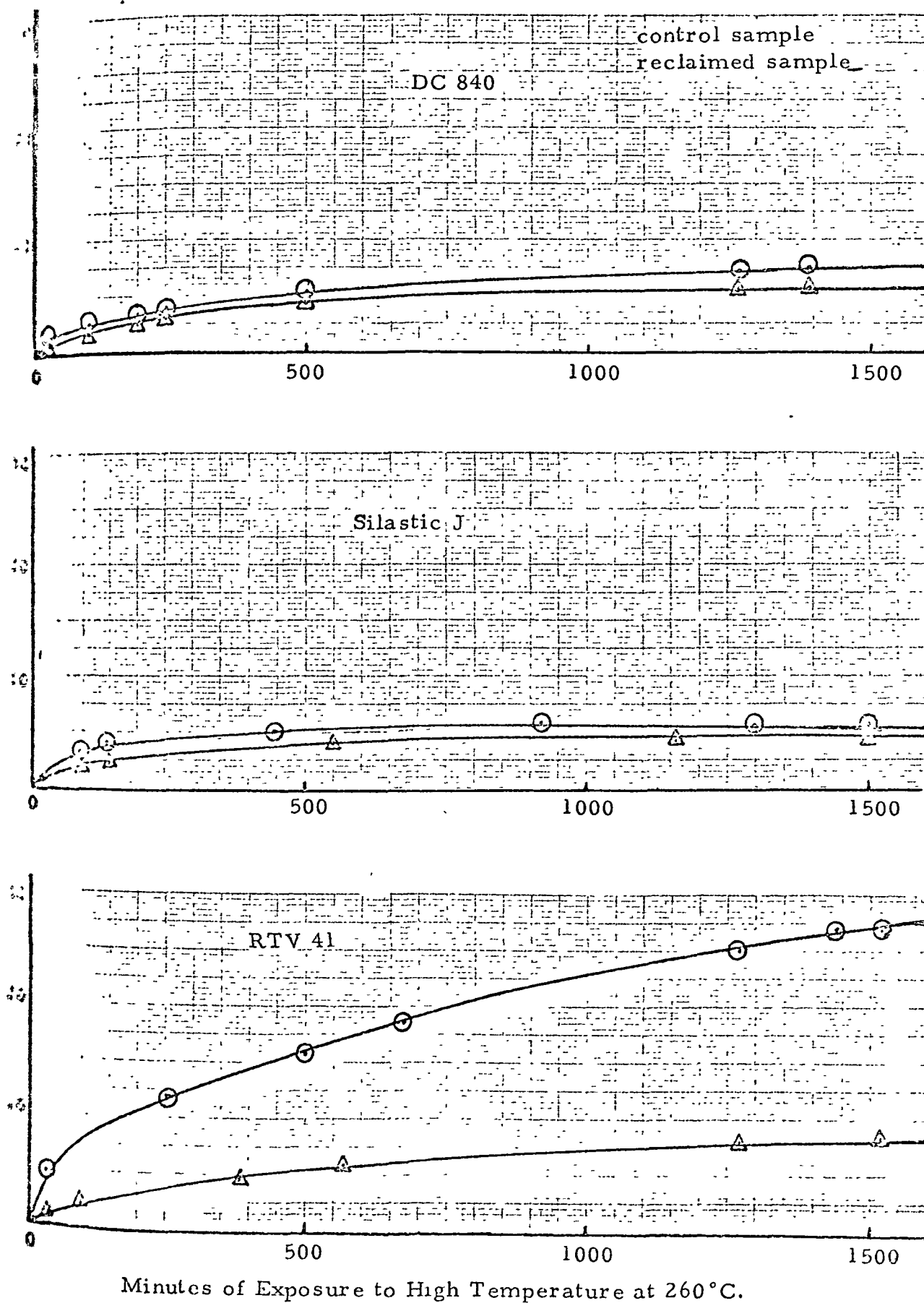
Table XIX. Film Properties of DC 840 Silicone Coatings

<u>Silicone resin</u>	<u>Sward Hardness</u>	<u>Flexibility</u> (1" Conical Mandrel)	<u>Reverse Impact</u> (inch-pound)
Control sample (DC 840 prepolymer baked 1 hr at 240°C	48	fail	2
Cured DC 840 dissolved in 1,2-diaminopropane	28	fail	2
Cured DC 840 dissolved in n-amylamine, n-propylamine (4:1)	44	fail	2
Cured DC 840 dissolved in diethyl amine	48	fail	3

* Control sample was baked at 240°C for 60 minutes. The other three samples were not baked but air dried for 10 days.

** One mil dry films on glass (Sward hardness) and steel panel (flexibility and reverse impact).

Figure IX. The Comparison of the Thermal Stability of Control Samples and Reclaimed Samples of Cured Silicone Polymers



SUMMARY

A non-sporicidal technique for solvent degradation of cured silicone polymers has been developed. The new technique shows substantial improvements in the quantitation of buried contamination as compared to the NASA standard recovery procedures. The high recovery of seeded spores from room temperature cured polymers indicates that the curing process is not sufficiently exothermic to reduce spore viability.

Non-sporicidal degradation of cured silicone polymers was studied by two different methods: (1) chemical degradation of cured silicone polymers by amine solvents at room temperature and, (2) mechanical degradation of solvent swollen samples using the concept of solubility parameter to select the best solvent for swelling. Viability studies were made using the first method. The chemical degradation of cured inoculated silicone potting compounds by n-butylamine solvent at room temperature was followed by serial dilution with benzene. A plate count technique which allowed the evaporation of amine solvent during the incubation gave a very high spore recovery (>90%). The mechanical degradation technique was not actually tested by spore recovery experiments; however, this method may be applicable to insoluble polymers used as potting compounds, coatings, adhesives and laminates on spacecraft.

The dissolution reaction of cured silicone polymers with amine solvents is proposed to be a bimolecular nucleophilic displacement. That is, the amine acts as a nucleophilic reagent attacking at the positive silicone atom of trifunctional units, $-O-\overset{\overset{R}{|}}{\underset{\underset{O}{|}}{Si}}-O-$. Attack at silicone atoms bonded to two oxygens is proposed to be much slower.

It is suggested that this selectivity explains why crosslinks are broken while straight segments are not depolymerized. Evidence for this proposed reaction was obtained by several different experiments:

(1) viscosity studies of silicone polymers in amine solution show that the viscosity of linear silicone polymer-amine solutions do not decrease as a function of time, while that of the crosslinked polymer (DC 840) solutions shows a decrease with time. This decreasing trend continues for the first 70-150 minutes, after which a constant viscosity is reached. These results indicate that the cured resin is degraded and suggests that cleavage of the polymer chain occurred primarily at the cross-linking or trifunctional silicone units, and not at the linear or difunctional silicone units. (2) The utilization of methanol to trap the silylamine showed evidence for the existence of the silylamine by NMR spectrophotometry. (3) The decreasing order of degradation power of amines is primary amine > secondary amine > tertiary amine. As in carbon bimolecular nucleophilic substitution reactions, steric effects are important here.

The dissolution of silicone polymers in amines suggested consideration of two applications, reclaiming used silicone polymers such as furniture molds and applying silicone coatings to heat sensitive substrates which cannot be subjected to current oven cure. In order to test the feasibility of these applications, experiments were conducted to determine extent of recrosslinking on solvent evaporation, thermal stability and physical properties of reclaimed polymers, and film properties of room temperature cured coatings.

The chemical structure of silicone polymers was determined by spectroscopic methods. The phenyl to methyl ratio, R/Si ratio, molecular weight, and hydroxyl content of the silicone resins were also determined.

RECOMMENDATIONS FOR FUTURE WORK

One interesting finding in this thesis is that cured silicone polymer can be dissolved in the amine solvents and that crosslinks reform during evaporation of amine solvents. With this in mind, the following further investigations are recommended:

- (1) Study of the reaction mechanism of amine-catalyzed degradation and reformation of organopolysiloxanes crosslinks possibly by kinetic methods,
- (2) Establishing a procedure for reclaiming used polymeric silicone material by dissolving the waste material in amines,
- (3) Designing a room temperature curing silicone coating system.

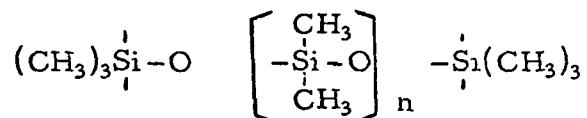
One of the greatest difficulties in the use of silicone resins for surface coating is that, currently, long times and high temperatures are required to complete the condensation.

APPENDIX

I. Structure of Silicone Polymers

A. IR Method

Infrared spectra were recorded for the octamethylcyclotetra- silane (D_4), silicone oil (DC Fluid 200), silicone rubber prepolymers (GE-RTV 41, DC Silastic J), and silicone resin prepolymers (DC 801, 802, 803, 804, 806A, 808, 840, GE-SR 112) as shown in Figures X to XXI. Characteristic absorption peaks which were pertinent to this investigation are listed in Table XX. The interpretation and comparison of the spectra of D_4 and DC 200 (Figures X and XI respectively) reveals that silicone oil DC 200 is a linear dimethyl polysiloxane polymer terminated by trimethylsilane.



In the IR spectrum, only $-\text{Si}-\text{O}-\text{Si}-$, $-\text{Si}(\text{CH}_3)_2$, $-\text{Si}(\text{CH}_3)_3$ present in the silicone oil show any absorption. Using only IR analysis, the existence of branched units is hard to determine. However, it is generally stated that silicone oils are linear polymers.

Room temperature curing silicone rubbers, RTV 41 (Figure XII) and Silastic J (Figure XIII) apparently are linear α, ω , -disilanol polydimethyl siloxanes which do not have H-Si bonds.

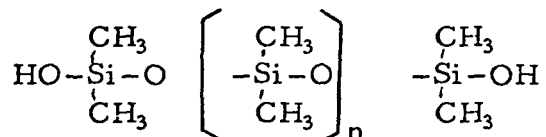


Table XX. Assignments for Major Infrared
Absorption Frequencies

Specific Absorption Frequency (cm^{-1})	Group Contribution		
3700-3200	Si-OH	Stretching	(97)
3250	Si-OH	Solid	(98)
3690	Si-OH	Solution	(98)
910-830	Si-OH	Associated with Si-O	
880-830	Si-OH	For silanol	
3400	Si-NH-Si	Stretching	(103)
1175 and 935	Si-NH-Si		
1280-1255	Si-CH ₃	CH ₃ deformation	(98, 87, 96)
860-760	Si-CH ₃	CH ₃ rocking	
765 (near)	Si-CH ₃	One methyl on Si	
855 and 800	Si-(CH ₃) ₂	Two methyls on Si	
840 and 765	Si-(CH ₃) ₂	Three methyls on Si	
1410 (near)	Si-CH ₃	Asymmetric CH ₃	
841 and 756-754	Si-(CH ₃) ₃	End groups	(96, 99)
1259	Si-(CH ₃) ₂	CH ₃ deformation	(100, 101)
814-800	Si-(CH ₃) ₂	CH ₃ stretching	(100)
700	Si-(CH ₃) ₂	Open chain or cyclic polysiloxanes	
800 (near)	Si-CH ₃	Stretch	(102)
850-800	Si-(CH ₃) ₂	Chlorosilanes	(96)
1125-1100	Si-C ₆ H ₅	Planar ring vibration	(97, 105, 104)
1116	Si-C ₆ H ₅	Characteristic of phenyl alkyl silane	
1100-1000	Si-O-Si	Asymmetric stretch	(96, 97, 98)
1085-1020	Si-O-Si	Long chain	
1020 (near)	Si-O-Si	Cyclotrisiloxane rings	
1090 (near)	Si-O-Si	Cyclotetrasiloxane rings	
1055-1024	Si-O-Si	Open chain	(96, 97, 98)
1068-1054	Si-O-Si	Branched chain	
1078-1076	Si-O-Si	Phenyl substitution	

Figure X. Infrared Spectrum of DC 200

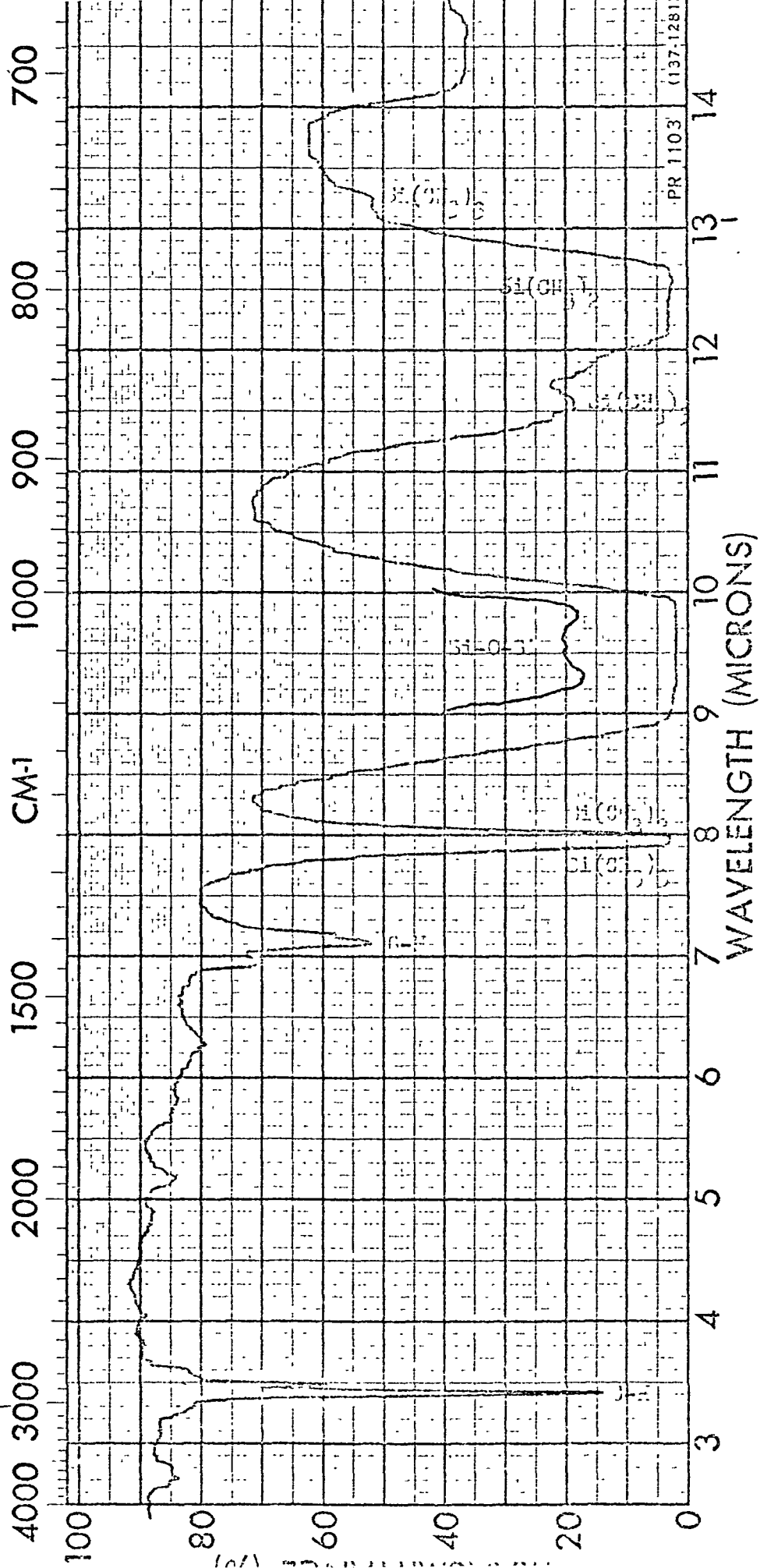


Figure XI. Infrared Spectrum of Octamethyltetracyclosiloxane

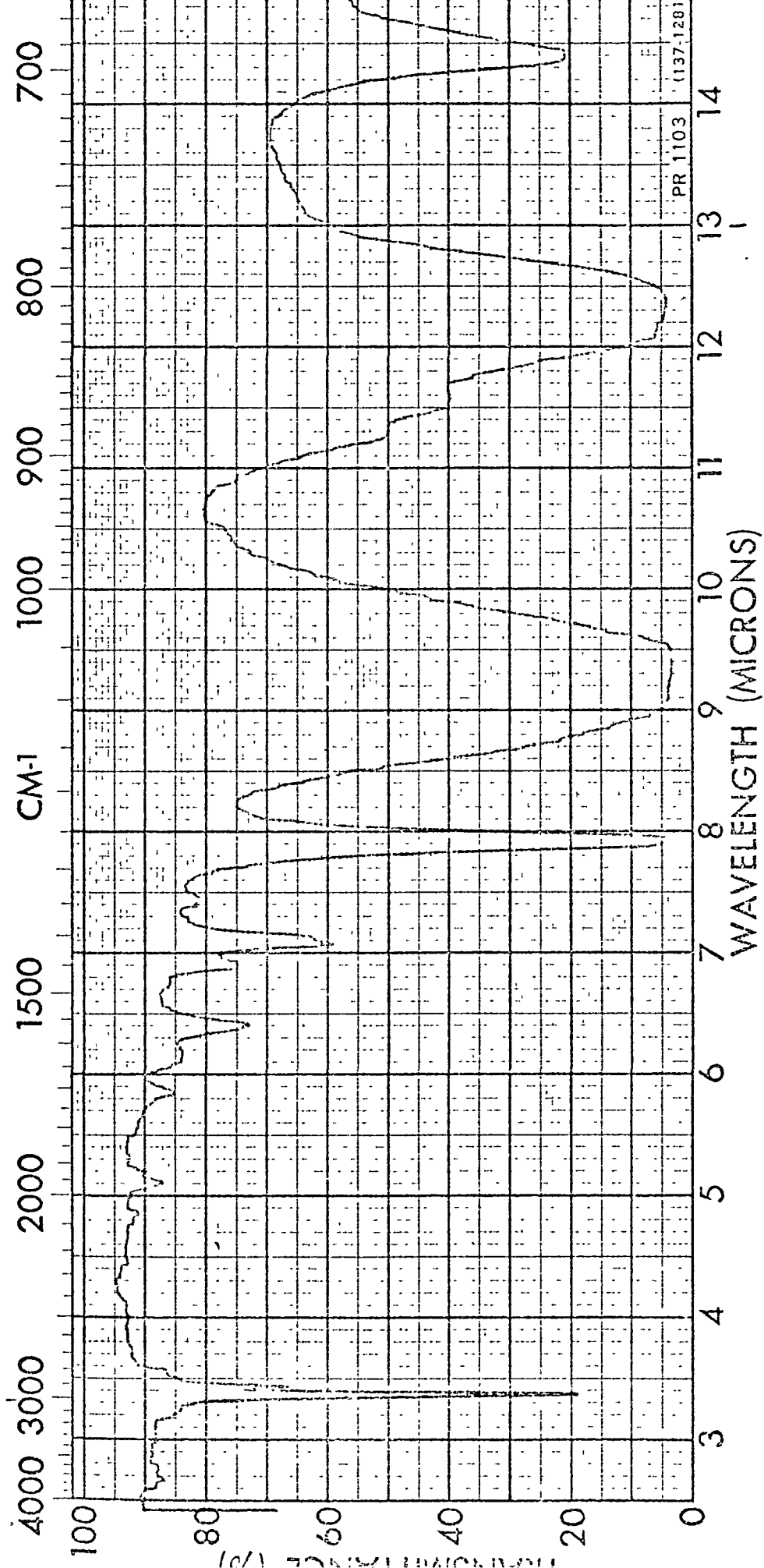


Figure XII. Infrared Spectrum of DC Silastic J

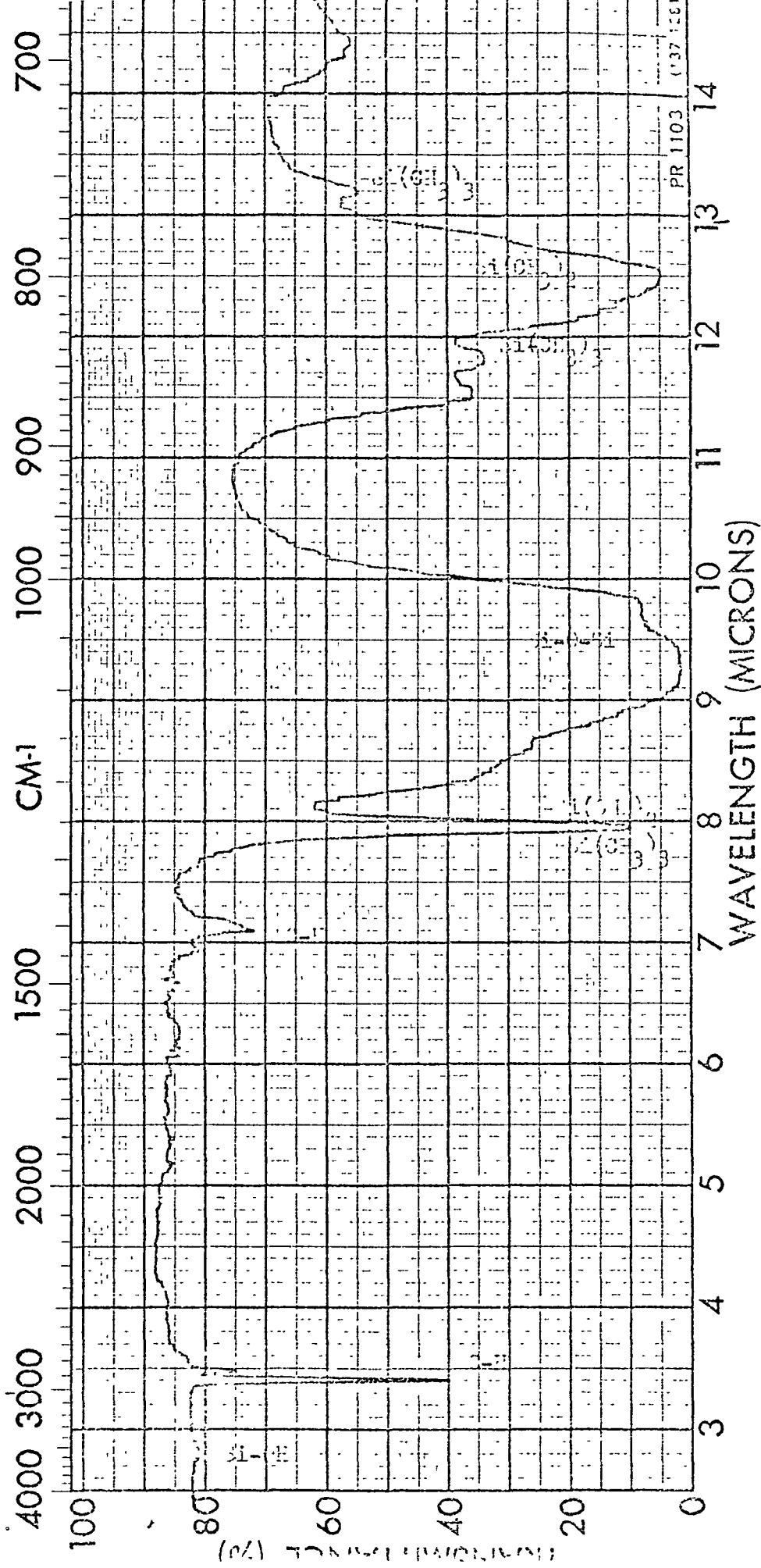


Figure XIII. Infrared Spectrum of GE-RTV 41

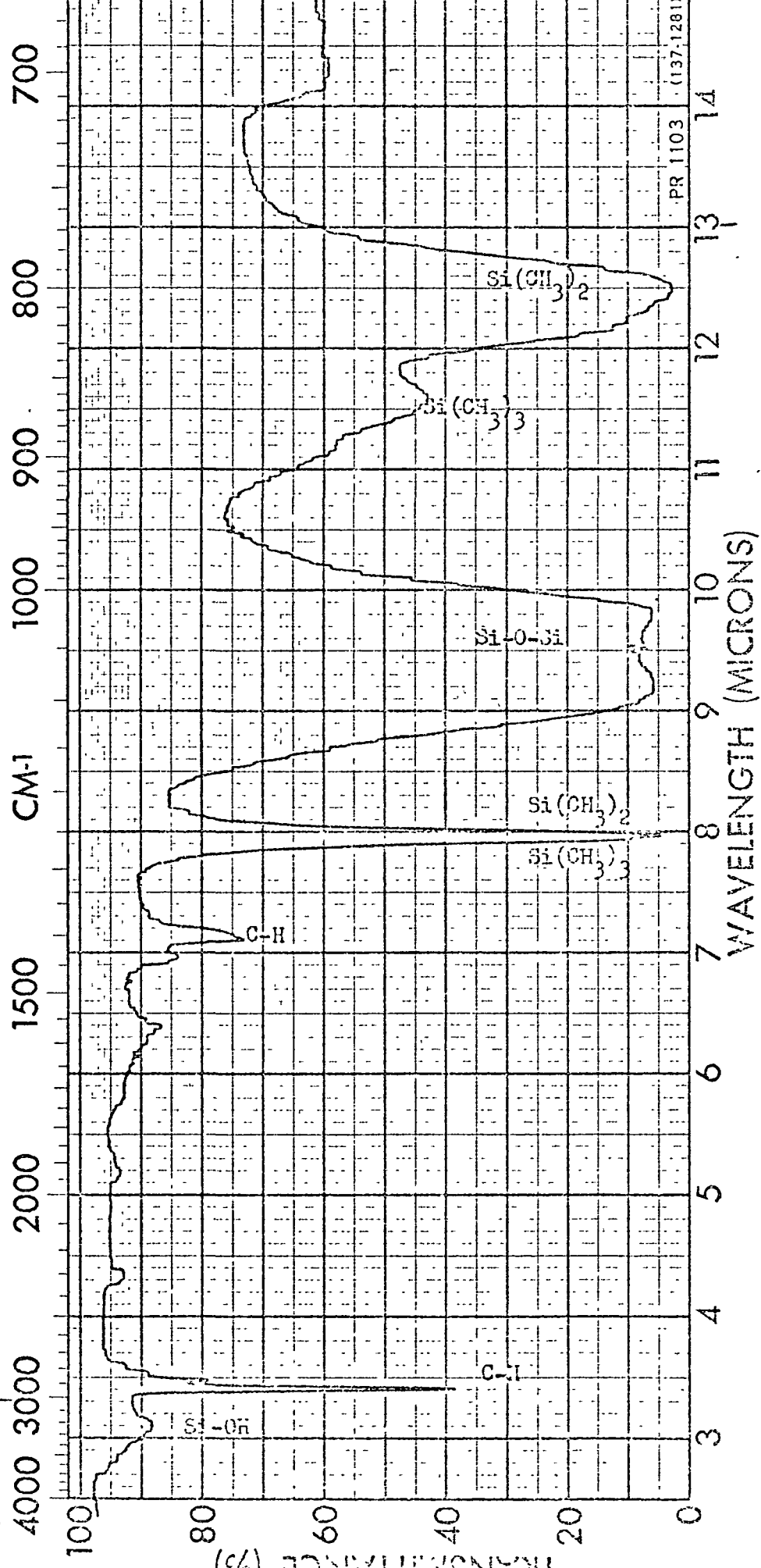


Figure XIV. Infrared Spectrum of DC 801

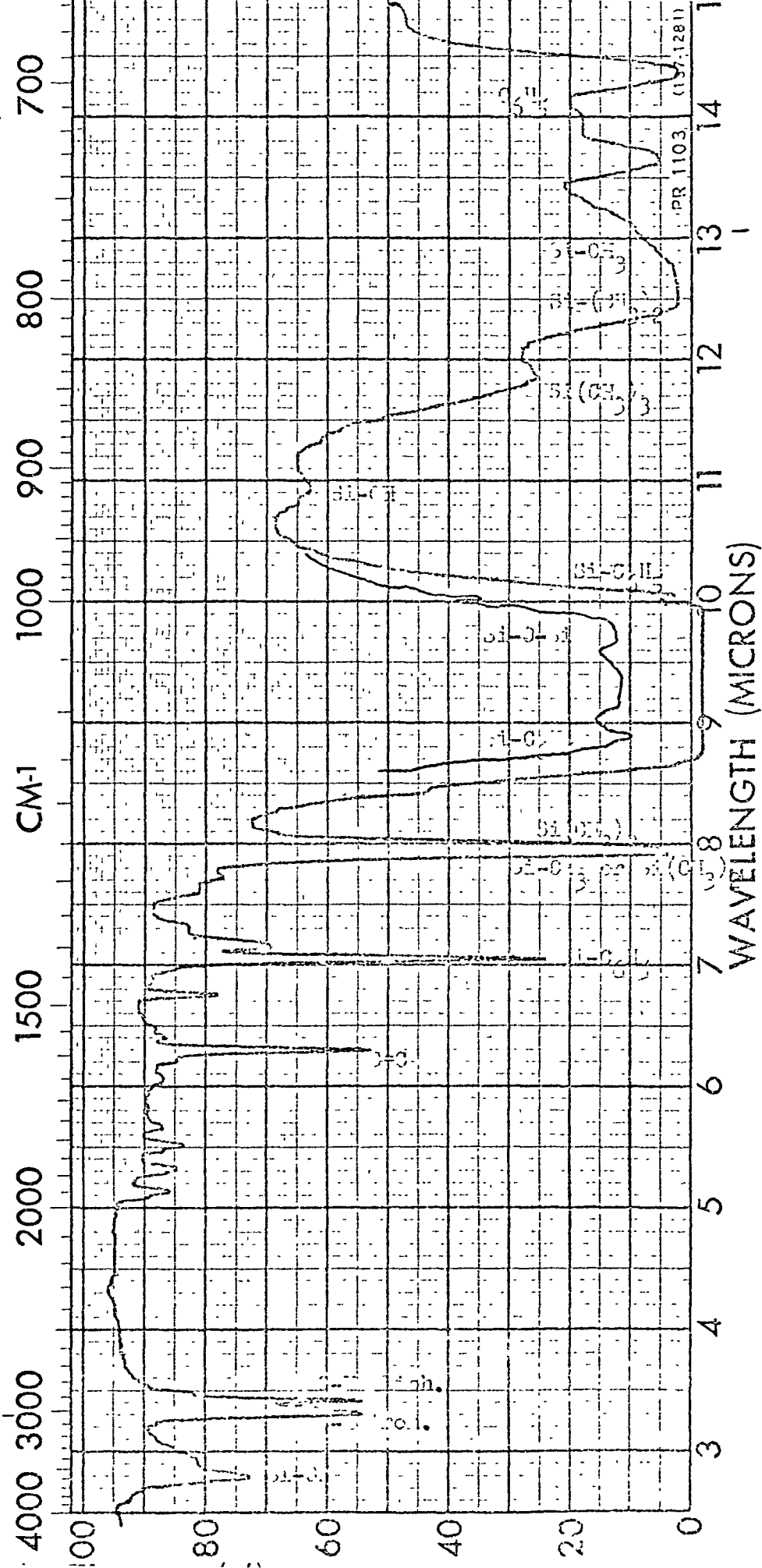


Figure XV. Infrared Spectrum of DC 802

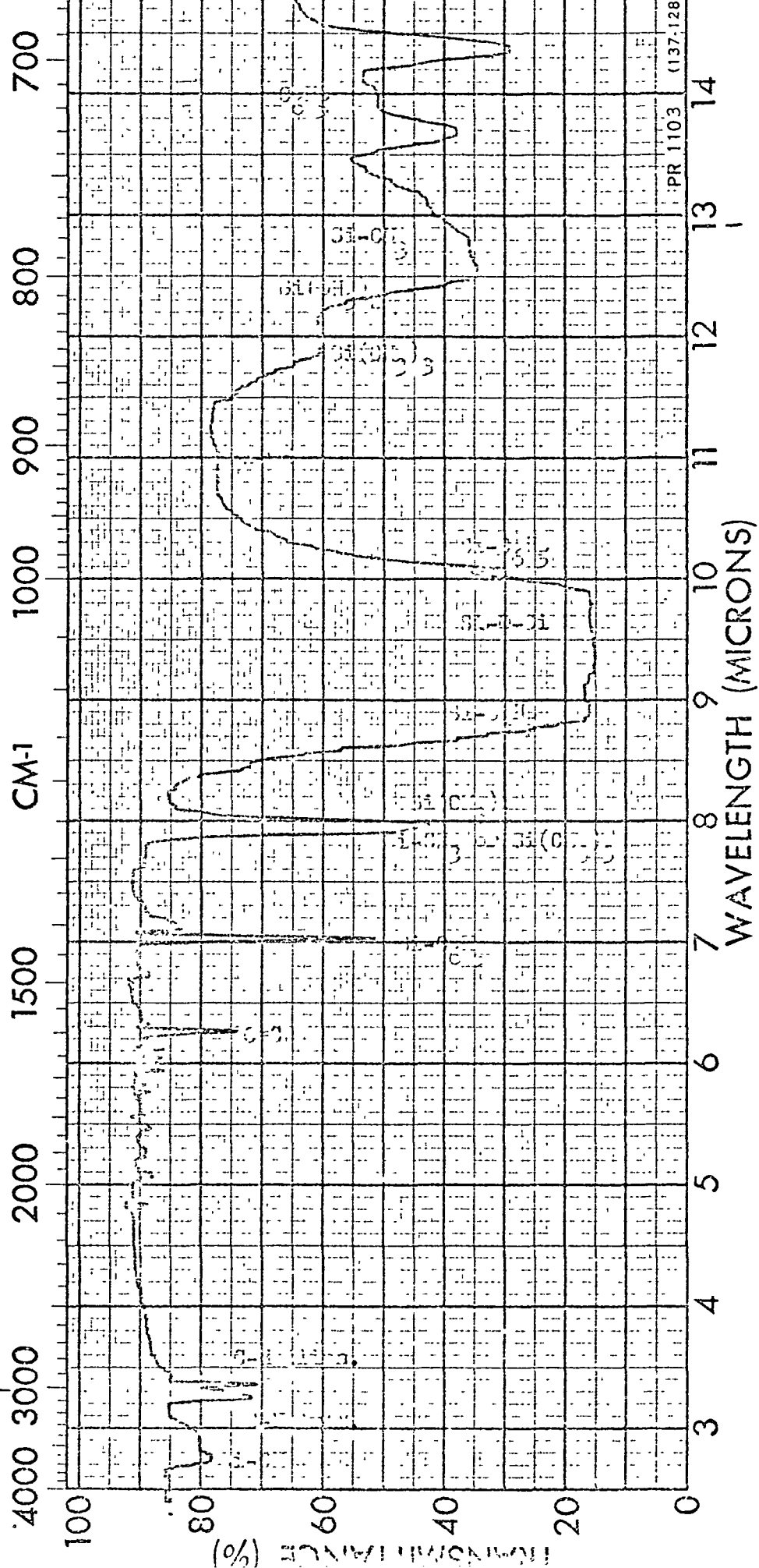


Figure XVI. Infrared Spectrum of DC 803

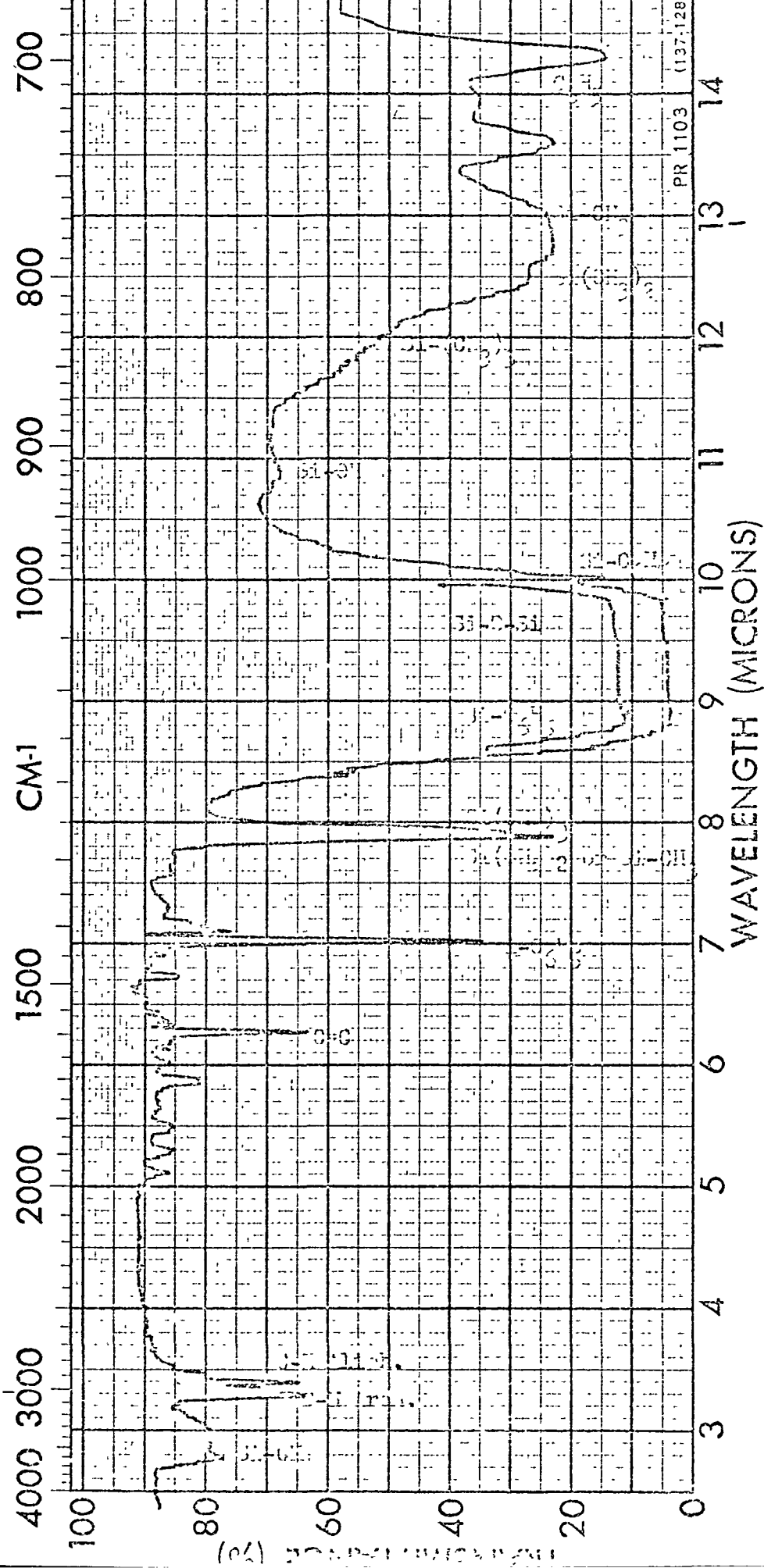


Figure XVII. Infrared Spectrum of DC 804

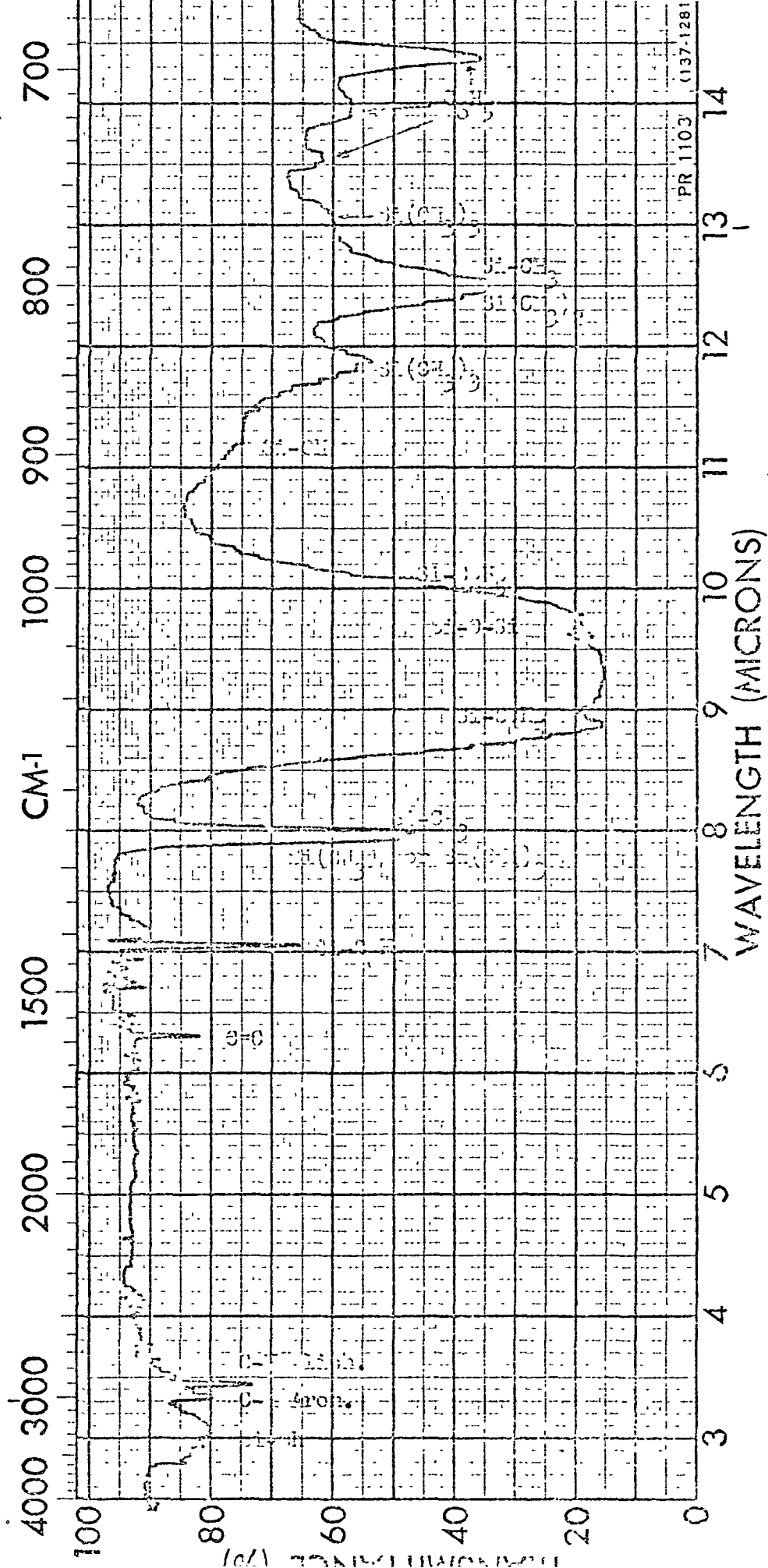


Figure XIX. Infrared Spectrum of DC 808

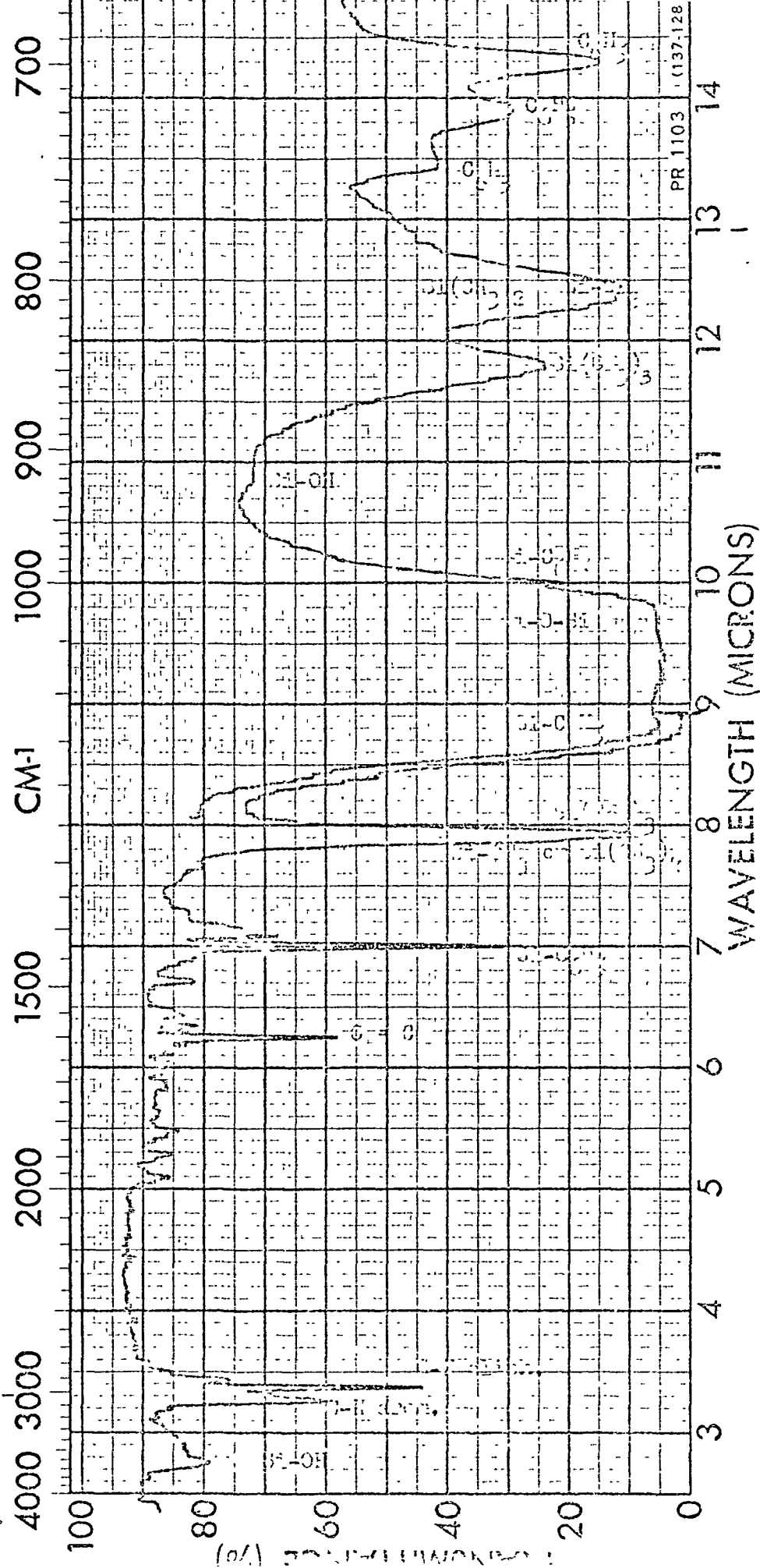


Figure XX. Infrared Spectrum of DC 840

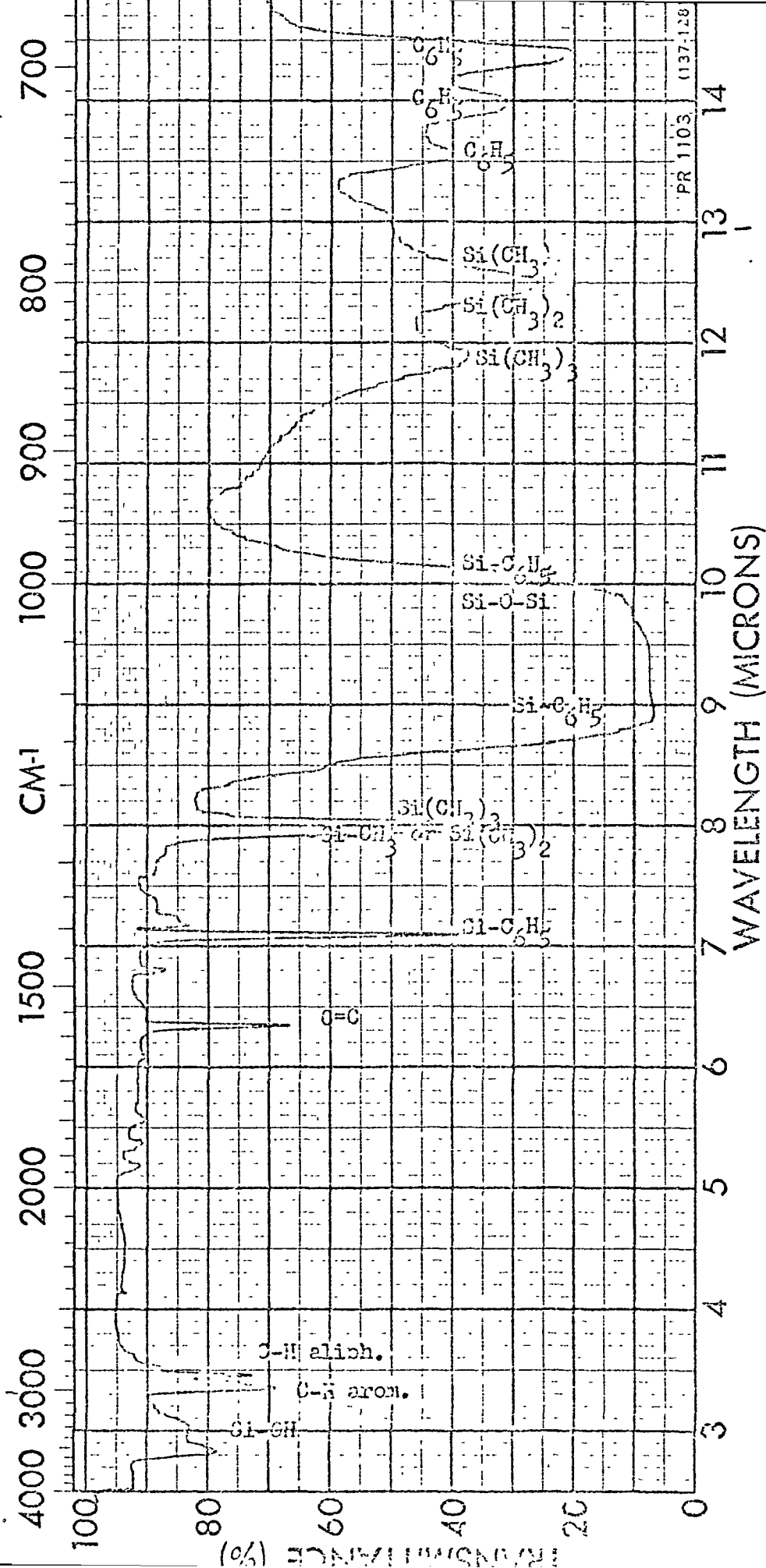
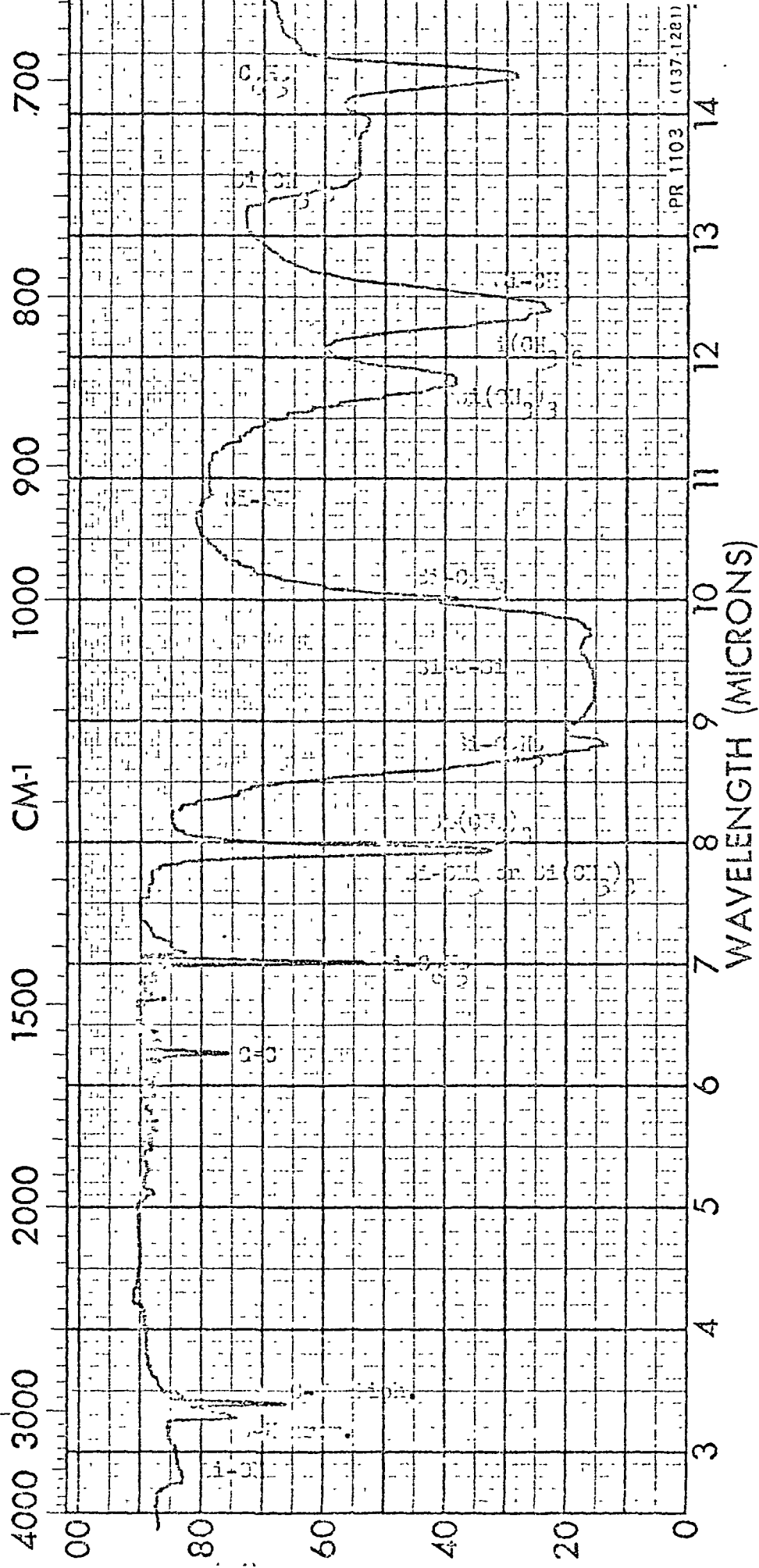



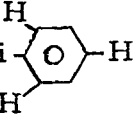
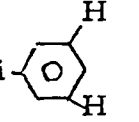
Figure XXI. Infrared Spectrum of GE-SR 112



All of the silicone resin spectra show no Si-OCH₃ or Si-C₂H₅ C-H symmetric stretching and no absorption characteristic of carbonyl. However, there are peaks for Si-O-Si, -Si-, Si-CH₃, and Si-OH as shown in Figures XIV to XXI. Therefore all the silicone resins studied here are polymethylphenyl siloxane polymers.

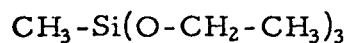
B. NMR Method

The NMR spectra gave the following results:

Sample	Peak (δ)	Assignment
D ₄	0.09	-Si-CH ₃
Silicone oil (DC 200)	0.11	-Si-CH ₃
Silicone rubbers (RTV 41, Silastic J)	0.09	-Si-CH ₃
Silicone resins (DC 840, 804)	0.12	-Si-CH ₃
	7.21	-Si- 
	7.5	-Si- 

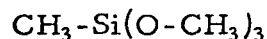
Sharp peaks from D₄ and the silicone oil DC 200 were obtained, and broad peaks from the silicone rubber as well as the silicone resins. The broad peak is attributed to the complexity of the polymer structure. According to the following reference data, (78) specific assignments of NMR peaks have been made to groups attached to Si. For example.

(a) methyltriethoxysilane



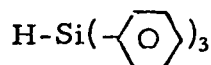
0.12 1.23 3.82

(b) methyltrimethoxysilane



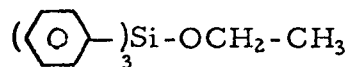
0.12 3.55

(c) triphenylsilane



5.48 7.3-7.4
 7.5-7.7

(d) triphenylethoxysilane



7.55-7.75 3.87 1.22
7.25-7.45

(e) Since silicone is electropositive relative to carbon, the electron density around the protons of Si-CH₃ is high. The tetramethylsilane peak is found at $\delta = 0$, the -O-Si(CH₃)₂-O- (open chain) peak at 0.17, and -O-Si(CH₃)₃ peak at 0.11

Therefore silicone oil (DC 200) can be identified as polymethylsiloxane; silicone rubber is also a polymethyl siloxane and silicone resins are polymethylphenylsiloxane polymers. There were no CH₃-O-Si peak (3.55), CH₃-CH₂-O-Si- peak (1.25 and 3.82), and H-Si- peak (5.48) in the silicone polymers studied here.

C. Hydroxyl Content of DC Silicone Resins

Determination of the hydroxyl number in the silicone resins was accomplished by using Fritz and Schenk's method of acid catalyzed acetylation of the organic hydroxyl groups (71). The results of this experiment are shown in Table XXI. There were some difficulties in the end point determination due to the high turbidities formed in the sample solution during titration. These difficulties may introduce some degree of error into the results. However, the use of a glass calomel electrode and pH meter minimizes the discrepancies in the end point determination.

Table XXI. Hydroxyl Content of DC Silicone Resins

<u>Silicone Polymer</u>	<u>% OH (grams OH/100 grams resin solids)</u>
DC 801	2.8
DC 802	0.6
DC 803	0.6
DC 804	4.2
DC 806A	0.5
DC 808	4.3
DC 840	0.6

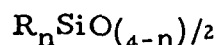
D. Phenyl to Methyl Ratio in DC Silicone Resins

Determination of the phenyl to methyl ratio in siloxane polymers was accomplished using the infrared spectroscopy method of Grant and Smith (73) and by NMR analysis. The results are shown in Tables XXII and XXIII. These two methods seem to agree with each other very well.

E. Determination of R/Si Ratio in DC Silicone Resins

As shown in Tables XXII and XXIII, the number of moles of phenyl groups and methyl groups in 100 grams of resin, as well as the ϕ/CH_3 ratio was determined. From this data, the ratio of R/Si was also mathematically determined as follows:

The composition of a siloxane unit is determined by the fact that each oxygen atom functions as a link between two silicon atoms so that each silicon can be considered to have only a half-share in each oxygen atom. The general formula of siloxane units of silicone resin which consist only of silicon, oxygen and hydrocarbon radicals is therefore



The actual organosiloxane units are represented by this formula with n values from 1 to 3. Here, n is the R/Si ratio or degree of substitution, which was calculated as shown below. The molecular weights of the parts of the units are:

$$\text{R}_n = \frac{(\text{mol. wt. of phenyl})(\phi/\text{CH}_3 \text{ ratio}) + (\text{mol. wt. of methyl})(1)}{\phi/\text{CH}_3 + 1} \times n$$

If ϕ/CH_3 ratio = A , then

$$\text{R}_n = \frac{77A + 15}{A + 1} \times n \quad (1)$$

$$\text{Si} = 28$$

$$\text{O} = 16 (4-n)/2 = 32 - 8n$$

Therefore the total mass of a siloxane unit is

Table XXII. Ratio of ϕ/CH_3 Determined by IR Method

Sample (prepolymer)	Average Peak Area of ϕ ($A_{3.2}$)	Average Peak Area of CH_3 ($A_{3.2}$)	$A_{3.2}/A_{3.4}$	ϕ/CH_3
DC 801	65	68	0.95	0.83
DC 802	70	72	0.97	0.83
DC 803	131	82	1.60	0.99
DC 804	40	75	0.54	0.43
DC 806A	72	55	1.30	1.17
DC 808	51	74	0.69	0.58
DC 840	85	65	1.32	1.19

Table XXIII. Number of Moles of Methyl and Phenyl Groups
per 100 g. of Dow Corning Silicone Polymers
Determined by NMR Method.

Samples (prepolymer)	Solvent	Internal Reference	No. of ϕ Groups	No. of CH_3 Groups	ϕ/CH_3
DC 801	CDCl_3	p-Dioxane	0.59	0.71	0.83
DC 802	CDCl_3	p-Dioxane	0.60	0.72	0.83
DC 803	CDCl_3	p-Dioxane	0.59	0.59	0.99
DC 804	CDCl_3	p-Dioxane	0.42	0.96	0.44
DC 806A	CDCl_3	p-Dioxane	0.65	0.55	1.19
DC 808	CDCl_3	p-Dioxane	0.53	0.90	0.59
DC 840	CDCl_3	p-Dioxane	0.64	0.54	1.17

$$\begin{aligned}
 R_n \text{SiO}(4-n)/2 &= R_n + \text{Si} + \text{O}(4-n)/2 \\
 &= \frac{(77A + 15)n}{1 + A} + 28 + 32 - 8n \\
 &= (77An + 15n + 60 + 60A - 8n - 8An)/1 + A \\
 &= [(7 + 69A)n + 60(1+A)]/1 + A \quad (2)
 \end{aligned}$$

The computation of n is continued by setting up a proportion

$$\frac{R_n}{R_n \text{SiO}(4-n)/2} = \frac{\text{wt. of } \phi \text{ and } \text{CH}_3 \text{ in 100 grams resin}}{100} \quad (3)$$

The molecular weights on the left side can be replaced by equations (1) and (2). From Table V one can obtain the number of moles of phenyl groups, p , and the number of moles of methyl groups, m , in 100 g; thus, the weight of alkyl groups in 100 grams is $(77p + 15m)$. Therefore, the proportion can be written as

$$\frac{\frac{(77A + 15)n}{1 + A}}{\frac{(7 + 69A)n + 60(1 + A)}{1 + A}} = \frac{77p + 15m}{100} \quad (4)$$

From equation (4) the only unknown factor, n , can be calculated. The values for the various polymers are tabulated in Table XXIV.

Table XXIV. R/Si Ratio of DC Silicone Resins

<u>Sample polymers</u>	<u>R/Si ratio</u>
DC 801	1.45
DC 802	1.50
DC 803	1.29
DC 804	1.27
DC 806A	1.41
DC 808	1.51
DC 840	1.37

F. Molecular Weight of DC 840

The number average molecular weight of DC 840 was determined by vapor pressure osmometry (72). Benzil was a standard for calibration of the osmometer and methylethyl ketone was the solvent.

The molecular weight of DC 840 was determined as $\bar{M}_n = 2,263$.

The results of molecular weight determination by the viscosity method are as follows:

With chlorobenzene as a solvent

$$\bar{M}_v = 127,000$$

$$\text{where } K = 3 \times 10^{-4}$$

$$\alpha = 0.62 \text{ (79)}$$

With n-butylamine as solvent

$$\bar{M}_v = 5940$$

$$\text{where } K = 2 \times 10^{-4}$$

$$\alpha = 0.72 \text{ (80)}$$

Vapor pressure osmometry measures the number average molecular weight, and viscometry gives the viscosity average molecular weight (where $\overline{M}_v = \overline{M}_w$). If the molecular weight distribution is normal, then

$$\overline{M}_n / \overline{M}_w = 1 / 1 + p \text{ where } p = \text{degree of polymerization}$$

and when $p \rightarrow 1$, then $\overline{M}_n = \overline{M}_w / 2$ using

the viscosity average molecular weight of 5,940 from above, the number average molecular weight is then calculated,

$$\overline{M}_n = \frac{\overline{M}_w}{2} = \frac{5,940}{2} = 2,970$$

These results do not agree with the results from the osmometry measurements. Molecular weight measurement by viscometry in this experiment seems to be inconsistent. It should be noted, however, that viscometry methods are suitable for the measurement of linear polymer molecular weights but not for the branched polymers.

LIST OF CHEMICALS

Acetone	Merck and Co., Inc.
Acetonitrile	J. T. Baker Co.
Acrylonitrile	J. T. Baker Co.
Amylamine	J. T. Baker Co.
Aniline	J. T. Baker Co.
Benzene	Merck and Co., Inc.
Benzonitrile	J. T. Baker Co.
1-Bromonaphthalene	J. T. Baker Co.
Butyl Acrylate	E. H. Sargent
Butylamine	Eastman Organic Chemical Co.
Butyl Cellosolve	E. H. Sargent
Carbitol	George T. Walker and Co.
Carbitol Acetate	E. H. Sargent
Carbon Tetrachloride	Matheson, Coleman and Bell
Cesium Hydroxide	E. H. Sargent
Chlorobenzene	Merck and Co., Inc.
DC-200 Silicone Oil	Dow Corning Chemical Co.
DC-801 Silicone Resin	Dow Corning Chemical Co.
DC-802 Silicone Resin	Dow Corning Chemical Co.
DC-803 Silicone Resin	Dow Corning Chemical Co.
DC-804 Silicone Resin	Dow Corning Chemical Co.
DC-806A Silicone Resin	Dow Corning Chemical Co.

DC-808 Silicone Resin

Dow Corning Chemical Co.

DC-840 Silicone Resin

Dow Corning Chemical Co.

1, 2 Diaminopropane

Aldrich Chemical Co.

1, 3 Diaminopropane

Aldrich Chemical Co.

Diethylamine

J. T. Baker Co.

Diethylene Glycol

George T. Walker and Co.

Diethylene Tetraamine

Union Carbide

Diethylene Triamine

Union Carbide

Diethylether Anhydrous

Mallinckrodt Chemical Works

Dimethylformamide

E. H. Sargent

Diisopropylamine

E. H. Sargent

Dimethylphosphate

J. T. Baker Co.

Dimethylsulfoxide

E. H. Sargent

Dipentene

Phillips Petroleum Co.

Ethyl Acetate

E. H. Sargent

Ethylamine

E. H. Sargent

Ethylenediamine

Matheson Coleman and Bell

Ethyl Acrylate

E. H. Sargent

Ethyl Benzoate

E. H. Sargent

Ethanol

U. S. Industrial Chemical Co.

Ethylene Carbonate

E. H. Sargent

Ethylene Diamine

Union Carbide

Ethylene Dichloride

Matheson, Coleman and Bell

Ethylene Glycol	George T. Walker and Co.
Formamide	J. T. Baker Co.
Glycerol	George T. Walker and Co.
Heptane	Phillips Petroleum Co.
Hexane	Phillips Petroleum Co.
Isopropyl Alcohol	J. T. Baker Co.
Lithiumhydroxide	J. T. Baker Co.
Methyl Acetate	E. H. Sargent
Methyl Alcohol	J. T. Baker Co.
Methyl Benzoate	E. H. Sargent
Methyl Cellosolve	E. H. Sargent
Methyl Ethyl Ketone	J. T. Baker Co.
Methyl Isobutyl Ketone	J. T. Baker Co.
Methyl n-Amyl Ketone	J. T. Baker Co.
Methyl Sulfone	E. H. Sargent
Mineral Spirits	Phillips Petroleum Co.
N-Ethylethylene Diamine	J. T. Baker Co.
Nitrobenzene	J. T. Baker Co.
Nitroethane	J. T. Baker Co.
Nitromethane	E. H. Sargent
p-Nitrophenol	Eastman Organic Chemical Co.
l-Nitropropane	J. T. Baker Co.
N-Methylaniline	J. T. Baker Co.

2-Nitropropane	J. T. Baker Co.
Octamethylcyclotetrasiloxane	Alfa Inorganic
N-Octyl Alcohol	J. T. Baker Co.
n-Propyl Alcohol	J. T. Baker Co.
n-Propylamine	J. T. Baker Co.
Iso-Propylamine	J. T. Baker Co.
p-Chlorotoluene	Matheson, Coleman and Bell
Potassium Hydroxide	E. H. Sargent
p-Dioxane	E. H. Sargent
Piperidine	Aldrich Chemical Co.
Pyridine	Aldrich Chemical Co.
Propylene Carbonate	E. H. Sargent
RTV-41 Silicone Rubber	General Electric Co.
RTV-60 Silicone Rubber	General Electric Co.
Rubidium Hydroxide	E. H. Sargent
Sec. Amyl Acetate	E. H. Sargent
Silastic "J" Silicone Rubber	Dow Corning Chemical Co.
Sec. Butylamine	Eastman Organic Chemical Co.
Sodium Hydroxide	E. H. Sargent
t-Butyl Alcohol	J. T. Baker Co.
t-Butylamine	Eastman Organic Chemical Co.
Tetrachloroethane	Matheson, Coleman and Bell
Tetraethylene Pentamine	Union Carbide

Tetrahydrofuran

E. H. Sargent

Tetralin

Merck and Co., Inc.

Toluene

Merck and Co., Inc.

Trichloroethane

Matheson, Coleman and Bell

1,1-2-Trichloroethane

Matheson, Coleman and Bell

Triethylene Tetraamine

Union Carbide

Turpentine

Phillips Petroleum Co.

Varsol 1

Phillips Petroleum Co.

BIBLIOGRAPHY

1. Lederberg, J. and Cowie, D. B., Science, 127, No. 3313, 1473, June 27, (1958).
2. Anon, Science, 128, No. 3329, 887, Oct. 17 (1958).
3. Anon, Nature, 183, No. 4666, 925, April 4 (1959).
4. Lederberg, J., Science, 132, No. 3424, 393, Aug. 12 (1960).
5. Biological Handbook for Engineers, NASA, CR-61237, June (1968).
6. Bruch, C. W., Koesterer, M. G., and Bruch, Mary K., Ind. Microbiol., 4, 334 (1963).
7. Heckly, R. J., Dimmick, R. L., and Windle, J. J., J. Bact., 85, 961 (1963).
8. McNall, E. G., and Duffy, W. T., "Microorganisms in Solid Materials, Phases I, II", Final Report, NAS7-100, JPL 950740 Jet Propulsion Laboratory, Pasadena, California (1965).
9. Hannan, P. J., "Electrophoretic Properties of Spores of Aspergillus Niger", Appl. Microbiol., 9 (1961).
10. Harden, V., and Harris, J. O., J. Bact., 65, 198 (1953).
11. Harris, J. O., J. Bact., 65, 518 (1953).
12. Harris, J. O., and Kline, R. M., J. Bact., 72, 530 (1956).
13. Hartman, R. S., Eigelsbach, J. B., Bateman, W., Braun, R., Herring, R., and Rodgers, R. D., Appl. Microbiol., 1, 178-183 (1953).
14. Phillips, C. R., and Hoffman, R. K., Science, 132, 991-995 (Oct. 14, 1960) p. 260-81.
15. Hoffman, R. K., Protection Branch Report of Test No. 7-60, Frederick, Md., Fork Detrick, Physical Defense Division (19 Dec. 1962).

16. Morelli, F. A., Research Summary No. 35-12 I, 14-16, Pasadena, California, Jet Propulsion Laboratory (Jan. 1962).
17. Portner, D.M., Protection Branch Report of Test No. 13-62, Frederick, Md., Fort Detrick, Physical Defense Division (8 Nov. 1961).
18. Mickle, H., J. Roy. Microscop. Soc., 68, 10-12 (1948).
19. Ross, J. W., Appl. Microbiol., 11, 33-35 (1963).
20. Bruch, C. W., Koesterer, M. G., and Bruch, Mary K., Ind. Microbiol., 4, 334 (1963).
21. Koesterer, M. G., NASA CR-56474, (Available from OTS, U. S. Dept. Comm.) (1964).
22. McNall, E. G., and Duffy, W. T., Final Report, NAS7-100, JPL 950740, Jet Propulsion Laboratory, Pasadena, California (1965).
23. "Microbial Cell Recovery From Solid Materials", Final Summary Report, Dynamic Science (14 May 1968).
24. Pflug, I. J., "Environmental Microbiology as Related to Planetary Quarantine", Semiannual Progress Report 6, June 1971, p. 41 (NASA Grant NGL 24-005-160).
25. Petersen, N. J., Abstract - Spacecraft Sterilization Technology Seminar (Jan. 1972), Task No. 193-58-63-12, Contract No. W-13,062.
26. Petersen, N. J., et al., "Release of Microbial Contamination from Fractured Solids", Space Life Sciences, 14, 532-537, (1969).
27. Pflug, I. J., Semiannual Progress Report 6, June 1971 (NASA Grant NGL-24-005-160).
28. Rheineck, A. E., and Heskin, R. A., "Quantitation of Buried Contamination by Use of Solvents", NASA Grant NGR 35-001-012, 1st Interm Report, Part I - Solvent Degradation of Amine Cured Epoxy Resins (Feb. 1972).

29. "Non-Metallic Materials Design Guidelines and Test Data Handbook, MSC-02681, NASA, May 29, 1970.
30. Hyde, J. F., Dow Corning, German Pat. 875,046 (US Prior 26, Feb. 1942).
31. Patnode, W. I., Thomson-Houston, French Pat. 938,822 (US. Prior 29, Oct. 1942).
32. Hyde, F., Warrick, E. L., and Fletcher, H. J., J. Amer. Chem. Soc., 68, 667 (1946).
33. George, P. D., and Zemany, P. D., Thomson-Houston French Pat. 117,4288 (US Prior 18, April 1956).
34. Gebhardt, J., Blengyel and F. ToRok, Mag. Kem., F. Folyoirat, 68, 159 (1962).
35. Bailey, D. L., and O'Connor, F. M., Union Carbide, U.S. Pat. 2881199 (14 Nov., 1956).
36. Voronkov, M. G., and Schabarova, Z. I., J. Gen. Chem. USSR (Engl. Transl.) 29, 1501 (1959).
37. Humphrey, B. J., and Wasserman, H. H., Connecticut Hard Rubber, U.S. Pat. 2673843 (17 May, 1951).
38. Hurd, D. T., and Kootsedes, G. J., German Pat. 954455 (US Prior 1 Sept. 1953).
39. Booth, H. S., and Freedman, M. L., J. Amer. Chem. Soc., 72, 2847 (1950).
40. Voronkov, M. G., Bull. Acad. Sci., USSR, Div. Chem. Sci. (Engl. transl.) 529 (1957).
41. Payne, D. S., J. Chem. Soc. (London), 1954, 2143.
42. Lewis, R. N., General Electric, U.S. Pat. 2500761 (19 June 1947).
43. Patnode, W. I., and Schmidt, F. C., J. Amer. Chem. Soc., 67, 2272 (1945).
44. Sommer, L. H., Pietrusza, E. W., and Whitmore, F. C., J. Amer. Chem. Soc., 68, 2282 (1946).

45. Sauer, R. O., J. Amer. Chem. Soc., 66, 1707 (1944).
46. Feher, F., Kuhlbornsch, G., Blumche, A., Keller, H., and Lippert, K., Chem. Ber., 90, 134 (1957).
47. Bailey, D. L., and O'Connor, F. M., Union Carbide, U. S. Pat. 2910496 (26 June 1956).
48. Hyde, J. F., Dow Corning, German Pat. 875046 (US Prior 26 Feb. 1942).
49. Hyde, J. F., Corning Glass Works, U. S. Pat. 2455999 (1 Aug 1944).
50. Barry, A. J., and Gilkey, J. W., Dow Corning, U. S. Pat. 2465188 (27 March 1948).
51. Hyde, J. F., Corning Glass Works, U. S. Pat. 2574265 (15 Nov. 1945).
52. Emeleus, H. J., and Onyszchuk, M. J., Chem. Soc. (London), 604 (1958).
53. McCusker, P. A., and Ostdick, T., J. Amer. Chem. Soc., 80, 1103 (1958).
54. Hurd, D. T., Dow Corning, German Pat. 873085 (US Prior 17 April 1950).
55. Orlov, N. F., Proc. Acad. Sci., USSR (Engl. transl.) 114, 629 (1957).
56. Schmidbaur, H., Angew. Chem., 77, 206 (1965).
57. Andrianov, K. A., and Kurasheva, N. A., Proc. Acad. Sci. USSR (Engl. transl.) 131, 297 (1960).
58. Kipping, F. S., and Hackford, J. E., J. Chem. Soc. (London) 99, 138 (1911).
59. Sauer, R. O., J. Amer. Chem. Soc., 66, 1707 (1944).
60. Jenkner, H., Kali-Chemic., German Pat. 954645 (5 May 1955).
61. Fritz, G., Z. Naturforsch., 106, 423 (1955).

62. Hall, L. B., and Swenson, B. L., "Spacecraft Sterilization by Destructive Heating", Presented at the COSPAR 12th Planetary Meeting, Prague, Czechoslovakia (11-24 May 1969).
63. Knox, W. E., Stumpf, P. K., Green, D. E., and Auerbach, V. H., J. Bact., 55, 451-8 (1948).
64. Michael, J. P., and Reid, R. D., "Microbiology" 2nd Edition.
65. Hildebrand, J. H., and Scott, R. L., Regular Solutions", Prentice Hall, Engelwood Cliffs (1962).
66. Burrell, H., "Interchemical Review", Vol. 14, No. 1, pp. 3-16, and No. 2, pp. 33-46 (1955).
67. "Elastomers in Adhesives", Technical Bulletin, E. I. Du Pont, March (1964).
68. Technical Bulletin 07-349, Dow Corning Co. (Dec. 1969).
69. Burkhard, C. A., Rochow, E. G., Booth, H. S., and Hart, Chemical Revs., 41, 97 (1947).
70. Osthoff, R. C., and Grubb, W. T., J. Amer. Chem. Soc., 76, 399 (1954).
71. Fritz, J. S., and Schenk, George H., Anal. Chem., 31, 1808 (1959).
72. Reuter, Hellmunt, Reichel, Gertraude (Inst. Silikon-und Fluorkarbon-Chem., Radebeul, Ger.) Plaste Kaut, 16 (9), 669-71 (1969).
73. Grant, G. D., and Smith, A. L., Analyt. Chem., 30, 1016 (1958).
74. Chamberlain, N. F., Anal. Chem., 31, 56 (1959).
75. Williams, R. B., Ann. N. Y., Acad. Sci., 70, 800 (1958).
76. Wirzing, G., "Naturwiss", 50, 466 (1963), 51, 211 (1964).
77. Damm, K., and Noll, W., Kolloid-Z, 158, 97 (1958).
78. Bhacca, N. S., Johnson, L. F., and Shoolery, J. N., "High Resolution NMR Spectra Catalog", Analytical Instrument Div. of Varian, National Press (1962).

79. Rafikov and Others, "Molecular-Weights and Polydispersity of Polymers", Daniel Davey and Co., Inc., New York, pp. 353 (1964).
80. Brandrup, J., and Immergut, E. H., "Polymer Handbook", Interscience Publishers, New York (1966).
81. Hendrickson, J. B., Hammond, G. S., and Cram, D. J., "Organic Chemistry", 3rd Edition, pp. 303, McGraw-Hill (1970).
82. Riddick, J. A., and Bunger, W. B., "Organic Solvents", Techniques of Chemistry, Vol. II, Wiley-Interscience, New York.
83. Doyle, C. D., and Schenectady, N. Y., U.S. Pat. 2575912 (20 Nov. 1951).
84. "Microbial Cell Recovery from Solid Materials", Final Summary Report, NASA Contract No. 950740, The Jet Propulsion Laboratory, Pasadena, Calif. (May 1968).
85. Hurd, D. T., Osthoff, R. C., and Corring, M. L., J. Amer. Chem. Soc., 76, 249 (1954).
86. Bazant, V., Chvalovsky, V., and Rathousky, J., "Organosilicone Compounds I", Academic Press, New York, pp. 42 (1965).
87. Swain, C. G., Esteve, R. M., and Jones, R. H., J. Amer. Chem. Soc., 71, 965 (1949).
88. Rochow, E. G., "Chemistry of the Silicones", John Wiley and Sons, New York, 2nd Edition, pp. 58 (1959).
89. Spieri, J. L., J. Amer. Chem. Soc., 74, 1003 (1952).
90. Langer, S. H., Connell, S., and Wender, I., J. Org. Chem., 23, 50 (1958).
91. Pike, R. M., J. Polymer Science, 50, 151 (1961).
92. Spiere, J. L., Dow Corning, U.S. Pat. 2676163 (3 Sept. 1952).
93. Pike, R. M., J. Org. Chem., 26, 232 (1961).
94. McDiarmid, A. G., "Advances in Inorganic Chemistry and Radiochemistry", Vol. 3, pp. (1961).

95. Eaborn, C., "Organosilicon Compounds", Butterworths Scientific Publications, pp.339 (1960).
96. Kuznetsova, A. G., Ivanov, V. I., Zavod, Lab., 37 (12) 1426-7 (Russ) (1971), Chem. Abstr., 76, 80891y (1972).
97. Voronkov and Schaparova, Z. I., J. Gen. Chem., USSR (Engl. transl.), 29, 1501 (1959).
98. Osthoff, R. C., Hurd, D. T., and Corrin, M. L., J. Amer. Chem. Soc., 76, 249 (1954).
99. Kucera, M., Jelined, M., Lanikova, J., and Vesely, K., J. Polymer Sci., 53, 311 (1961).
100. Riddick, J. A. and Bunger, W. B., "Organic Solvents", Techniques of Chemistry, Vol. II, Wiley-Interscience, New York 1970.
101. Noll, W. K., Damm and Krauss, W., Farbe und Lack, 65, 17 (1959).
102. Clark, H. A., Dow Corning, Brit. Pat. 675912 and 689648 (US Prior 2, Sept. 1949).
103. Wright, N., and Hunter, M. J., J. Amer. Chem. Soc., 69, 803 (1947).
104. Smith, A. L., Spectrochem. Acta., 16, 87 (1960).
105. Richards, R. E., and Thompson, H. W., J. Chem. Soc., 124 (1949).
106. Clark, H. A., Gordon, A. F., Young, G. W., and Hunter, M. J., J. Amer. Chem. Soc., 73, 3798 (1951).
107. Smith, A. L., J. Chem. Phys., 21, 1997 (1953).
108. Young, C. W., Koehler, J. S., and McKinney, D. S., J. Amer. Chem. Soc., 69, 1410 (1947).
109. Rank, D. H., Saksena, B. D., and Shull, E. R., Dis. Faraday Soc., 69, 1410 (1947).
110. Tessenden, J. Org. Chem., 25, 2191 (1960).
111. Harvey, M. C., Nebergall, W. H., and Peak, J. S., J. Amer. Chem. Soc., 76, 4555 (1954).

112. Kniseley, R. N., Fassel, V. A., and Conrad, E. E., Spectrochem. Acta., 15, 651 (1969).